Chapter 3

SEMICONDUCTOR OXIDES MEDIATED PHOTOCATALYTIC DEGRADATION OF PHENOL IN WATER

3.1 Introduction

Phenol, as stated in chapters 1 and 2, is a major pollutant found in effluent streams from various chemical industries producing resins, plastics, textiles, pulp paper, etc., and is often used as a model pollutant in wastewater remediation studies. Even at low concentration, it is considered to be toxic and is not allowed to be discharged directly into surface waters or to the normal sewage system. Semiconductor photocatalysis has emerged as an important destruction technology for the mineralization of organic pollutants in water resulting in CO₂, H₂O and mineral acids or their salts as end products.
In this chapter, the photocatalytic activity of ZnO, TiO₂ and ZnO-TiO₂ for the degradation of trace amounts of phenol in water is evaluated under various reaction conditions and in presence of various additives. Over the years, a large number of semiconductors have been reported as potential photocatalysts. The most widely studied among them are TiO₂, ZnO and CdS. In fact, TiO₂ has been one of the most active photocatalysts reported so far and has become the bench mark against which photocatalytic activity of other semiconductors is measured. ZnO is a suitable alternative to TiO₂ and is in fact more efficient than TiO₂ for several applications. Similarly, coupled semiconductor systems such as CdS/TiO₂, ZnO/Fe₂O₃ and ZnO/TiO₂ have also been reported to modify the photocatalytic activity of their constituents. [56, 57, 87,130,131]. In this chapter, the photocatalytic degradation of phenol and its mineralization on ZnO, TiO₂ and ZnO/TiO₂ are investigated in detail. The fate of H₂O₂ formed concurrently is also monitored which provided fresh insight for the first time into the inconsistency reported with respect to the amount of H₂O₂ formed in photocatalytic systems.

3.2 Experimental Details

3.2.1 Materials

Phenol AnalaR Grade (99.5% purity) from Qualigens (India) was used as such without further purification. ZnO and TiO₂ used in the study were supplied by Merck (India) Limited. In both cases, the particles were approximately spherical and non-porous with a purity of over 99%. H₂O₂ (30% W/V) used was from Ramkem Limited (India). The water used for all experiments was purified by double distillation. Other chemicals used
such as NaCl, NaI, Na₂SO₄, Al₂O₃, Fe₂O₃, NaF, Na₂CO₃, NaNO₃, NaBr and Na₃PO₄·12H₂O were of Reagent grade and used as such without further purification. ZnO/TiO₂ composites were prepared by thorough physical mixing of required amounts of ZnO and TiO₂ catalysts for 30 minutes.

### 3.2.2 Analytical Procedures

The concentration of phenol in routine experiments was followed by spectrophotometry. At periodic intervals, samples were drawn from the reactor, centrifuged and the centrifugate was analysed for the concentration of phenol left behind. The analysis is based on the reaction of phenolic compounds with 4-amino antipyrene at pH 7.9 ± 0.1 in presence of potassium ferricyanide to form a coloured antipyrene dye. The absorbance of this dye solution is measured at 500 nm using a spectrophotometer (Varian UV-VIS spectrophotometer). A similar reaction system kept in the dark under exactly identical conditions but without UV irradiation was used as the reference. The major intermediates of phenol degradation before ultimate mineralization were verified by high performance liquid chromatography (Microbondapack C18 column of 36 cm length. Eluting solvent was water-acetonitrile in the ratio 80:20, UV detector). The identified intermediates such as catechol, hydroquinone and benzoquinone are not consistently detected or detected only in negligible quantities by HPLC analysis, indicating that they undergo faster/ comparable degradation in relation to the parent compound. Hence, they are not expected to interfere in the spectrophotometric analysis of phenol.
Surface area of the catalysts was measured using BET method using TriStar 3000.V6.07A. The X-ray diffraction (XRD) measurements were made using Rigaku X-ray diffractometer with Cu-Kα radiation. Scanning Electron Microscopy (SEM) measurements were performed using JEOL Model JSM-6390 LV. Total organic carbon content of reaction solution was recorded using the TOC Analyzer Vario TOC CUBE (Elementer Analysen systeme make).

H₂O₂ was analyzed by iodometry. The oxidation of iodide ions by H₂O₂ generated in situ was carried out in 1N sulphuric acid in presence of a few drops of saturated ammonium molybdate solution, which acts as a catalyst. The reaction was allowed to go to completion (5 minutes) in the dark. The liberated iodine was then titrated against a standard solution of sodium thiosulphate of concentration 2 × 10⁻³M prepared freshly from 10⁻¹M stock solution. Freshly prepared starch was used as the indicator. Mineralization was identified from the evolution of CO₂ after prolonged US irradiation. CO₂ was detected by the precipitation of BaCO₃ when the gas phase above the reaction suspension flushed with O₂ was passed through Ba(OH)₂ solution. In addition, TOC in the mixture was determined using the TOC analyzer to confirm the complete mineralization.

### 3.2.3 Adsorption

A fixed amount (0.1 g) of the catalyst was introduced into 50ml of phenol solution of required concentration in a 100 mL beaker and the pH was adjusted as required. The suspension was agitated continuously at a constant temperature of 29 ± 1°C for 2 hrs to achieve equilibrium. This was then centrifuged at 3000 rpm for 10 min. After centrifugation, the concentration
of phenol in the centrifugate was determined spectrophotometrically. The adsorbate uptake was calculated from the relation:

$$q_e = \frac{(C_0 - C_e) V}{W}$$ ................................................... (31)

where $C_0$ is the initial adsorbate concentration (mg/L), $C_e$ is the equilibrium adsorbate concentration in solution (mg/L), $V$ is the volume of the solution in litre, $W$ is the mass of the adsorbent in gram and $q_e$ is the amount adsorbed in mg per gram of the adsorbent at equilibrium.

3.2.4 Photocatalytic Experimental set up

In a typical experiment, required amount of the catalyst is suspended in an aqueous solution of phenol of desired concentration in the reactor. Simple glass beakers (250 ml) were used as reactors in routine experiments. The beakers were placed in a water bath through which water at the required temperature was circulated. The catalyst substrate suspension was continuously mixed using a magnetic stirrer. The suspension was illuminated with a 400W super high-pressure mercury lamp mounted above the system [Fig. 3.1(a)]. For specific experiments specially designed jacketed reactor [Fig. 3.1(b)] was used. This reactor has provision for circulation of water in the jacket and bubbling gas through the suspension. At periodic intervals, samples were drawn, the suspended catalyst particles were removed by centrifugation and the concentration of phenol left behind was analyzed as explained under analytical procedure. In this case also, a similar reaction system kept in the dark under exactly identical conditions but without UV irradiation was used as the reference. The samples were also analysed for the presence of $\text{H}_2\text{O}_2$ and quantified the same as and when required. For the identification
of intermediates, higher concentration of phenol [1000 ppm] and higher loading of catalyst were used in the experiments. The irradiation is done upto ~ 50% degradation of phenol and the solution was analysed by HPLC for the intermediates. Similarly, for confirming the mineralization, evolution of CO₂, at higher concentration of phenol and higher loadings of catalyst was measured.

Fig.3.1(a): A schematic diagram of the photocatalytic experimental set up.

3.3 Results and Discussion

3.3.1 Catalyst characterization and Preliminary experiments

The catalysts ZnO and TiO$_2$ used in the study were characterized by surface area, particle size analysis, pore size distribution, adsorption, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The pore size distribution is shown in Fig. 3.2 (a & b).

![Pore size distribution of ZnO.](image)

![Pore size distribution of TiO$_2$.](image)

The XRD patterns of TiO$_2$ (anatase), TiO$_2$ (rutile), TiO$_2$ (commercial) containing anatase and rutile form, ZnO and composite ZnO-TiO$_2$ with a
molar proportion of 4:6 are shown in Fig. 3.3 (a, b, c, d & e) respectively. The characteristic diffraction peaks of rutile, anatase as well as the commercial sample showed that the TiO$_2$ contains approximately 75% anatase and 25% rutile. In the case of ZnO, three sharp peaks are found from 30 to 40° with very high intensity. These diffraction peaks are also found in the XRD pattern of composite ZnO-TiO$_2$ powder [3.3 (e)]. The composite powder contains the two crystalline phases belonging to anatase TiO$_2$ and ZnO. The surface areas of TiO$_2$ and ZnO, as determined by the BET technique, were approximately 15 m$^2$/g and 12 m$^2$/g respectively. Fig. 3.3 (f, g & h) gives the SEM images of the samples mentioned above. The average particle size of both TiO$_2$ and ZnO was approximately in the range 0.1 to 4.0 µm. Average dynamic particle size as determined by Malvern mastersizer is 3.2 µm.

![Fig.3.3(a): XRD pattern of TiO$_2$ (Anatase).](image)
Fig. 3.3(b): XRD pattern of TiO$_2$ (Rutile).

Fig. 3.3(c): XRD pattern Commercial TiO$_2$ (Anatase and Rutile).
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Fig. 3.3(d): XRD pattern of ZnO.

Fig. 3.3(e): XRD pattern of ZnO-TiO$_2$.
Fig.3.3(f): SEM image of TiO$_2$.

Fig.3.3 (g): SEM image of ZnO.
Fig. 3.3 (h): SEM image of ZnO-TiO₂

Preliminary investigations on the photocatalytic degradation of phenol were made using ZnO, TiO₂, and ZnO-TiO₂ catalysts under identical conditions. The results are shown in Fig. 3.4. ZnO, TiO₂ and ZnO-TiO₂ (1:1 w/w) yielded 55%, 63% and 67% degradation of phenol respectively in 2 hr irradiation time.
Experiments conducted in the absence of either catalyst or light showed no significant degradation of phenol suggesting that both catalyst and light are essential for the degradation. This is expected on the basis of the general mechanism of photocatalysis. Photoexcitation of the semiconductor, results in the formation of an electron–hole pair on the surface of catalyst. These electrons and holes are responsible for the production of hydroxyl radical species that interact with the pollutants, degrade and eventually mineralize them. Both ZnO and TiO₂ have comparable photocatalytic efficiency (55% and 63%), though TiO₂ is slightly more active. Combining them does not modify the efficiency significantly as seen in Fig. 3.4. The adsorption study at the respective optimum dosage of catalyst (Section 3.3.2) shows that TiO₂ is a better
adsorbent compared to the other two catalysts i.e. 3.6, 8.8 and 4.4 mg/g for ZnO, TiO₂ and ZnO-TiO₂ respectively.

Fig. 3.5 shows the efficacy of ZnO/TiO₂ at various weight ratios for the photodegradation of phenol under identical conditions. The percentage degradation varied slightly with the composition of ZnO-TiO₂. Maximum degradation of 67% is observed at the ratio 4:6 (ZnO-TiO₂).

Pure TiO₂ powder (Zn/Ti = 0:1) gives ~ 63% degradation of phenol under UV irradiation and the corresponding adsorption (8.8 mg/g) of phenol is also the highest. The degradation of phenol in presence of TiO₂ is not affected by addition of ZnO upto 20%. Thereafter it slowly increases with increase ZnO concentration, reaches an optimum at the ratio 4:6 (ZnO-TiO₂).
and slowly decreases or stabilizes. The inter-particle electron transfer (IPET) in coupled ZnO-TiO$_2$ [132] which is reported to be responsible for the higher photocatalytic activity of coupled ZnO-TiO$_2$ is not fully seen here though its contribution cannot be completely ruled out. Since TiO$_2$ is slightly more active compared to ZnO, the modest improvement in efficiency in presence of the latter can be attributed to the IPET and better absorption of light.

3.3.2 Effect of catalyst dosage

Optimizing catalyst concentration is important in order to avoid the uneconomical use of catalyst and to ensure maximum absorption of photons. Hence, the effect of catalyst dosage on the photocatalytic degradation of phenol is studied at different loadings of ZnO, TiO$_2$ and ZnO-TiO$_2$ (4:6) keeping all other parameters constant. The results are shown in Fig. 3.6.

![Fig. 3.6: Effect of catalyst loading on the photocatalytic degradation of phenol over ZnO, TiO$_2$ and ZnO-TiO$_2$.](image)
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It is seen that in all three cases, increase in the catalyst loading from 0.02 to 0.10 g/L increases the phenol degradation fairly sharply followed by a slow and steady decrease and eventual stabilization at higher loadings. This is characteristic of many such reactions in heterogeneous photocatalysis [57,130,133-141].

The degradation efficiency is higher at the higher catalyst loading, due to the efficient absorption of light and increased number of adsorption sites available which lead to the formation of higher number of reactive hydroxyl radicals and their interaction. Higher amount of catalyst loading may lead to more efficient utilization of incident photons striking the catalyst surface. Also there will be more number of active sites for adsorption of phenol as well as generation of Reactive Oxygen Species (ROS) at the surface. However, increase in the catalyst concentration beyond the optimum will result in the scattering and reduced passage of light through the sample. Another reason may be the aggregation of catalyst particles causing a decrease in the number of available active surface sites. The particles cannot be fully and effectively suspended beyond a particular loading in a particular reactor which also leads to suboptimal penetration of light and reduced adsorption of the substrate on the surface. At higher loading, the catalyst has a tendency to settle at the bottom of the reactor. It is also possible that at higher loading, part of the originally activated semiconductor is deactivated through collision with ground state catalyst according to the equation [56, 57, 59, 130, 131,142].

\[
\text{MO}^* + \text{MO} \rightarrow \text{MO}^d + \text{MO} \quad \text{................................................. (32)}
\]

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Where, MO is semiconductor oxide such as ZnO, TiO$_2$ and ZnO-TiO$_2$. MO* and MO* are its activated and deactivated forms respectively. All those factors together contribute to a decrease in the efficiency of the catalyst beyond the optimum level.

All further studies were done using the optimum loading of 0.1 g/L for all three catalysts, i.e., ZnO, TiO$_2$ and ZnO-TiO$_2$.

**3.3.3 Effect of irradiation time**

The effect of irradiation time on the photocatalytic degradation of phenol is shown in Fig.3.7. The percentage degradation of phenol increases as the irradiation time increases. The mixed catalyst, ZnO-TiO$_2$, has better degradation efficiency than the individual components i.e. ZnO and TiO$_2$ throughout the irradiation period. The percentage removal reaches an optimum and levels off with time. As the time increases, the concentration of phenol available for interaction with the surface decreases. Also some of the active sites on the catalyst surface will be covered by the reaction intermediates. The availability of oxygen also is affected due to depletion of adsorbed as well as dissolved oxygen. The composition of the system also becomes complicated with too many products which reduces the effectiveness of penetration of light. Hence, the degradation reaches a plateau which can be broken only by modifying the reaction conditions.
3.3.4 Effect of concentration

The effect of initial concentration of phenol on the rate of its photocatalytic degradation in presence of ZnO, TiO₂ and ZnO-TiO₂ catalysts was studied, by varying the concentration over the range of 10–60 mg/L in presence of 0.1g L⁻¹ catalyst under UV light. The results are shown in Fig. 3.8(a).
Fig. 3.8(a): Effect of concentration of phenol on its photocatalytic degradation over ZnO, TiO$_2$ and ZnO-TiO$_2$.

The rate degradation of phenol increases with increase in concentration in all cases. The rate slows down and eventually stabilizes in the case of pure ZnO and TiO$_2$ at 30 and 40 mg/L respectively. However, the rate continues to increase even at higher concentration of phenol in the case of ZnO-TiO$_2$ combination.

At higher concentration of substrate beyond the optimum, it may be presumed that active sites are fully covered by the phenol molecule and its degradation intermediates. Hence the ability of the surface to absorb light and to generate more electron-hole pairs is reduced. This reduces the photodegradation efficiency of this catalyst. As the phenol concentration is increased, there is a decrease in the path length of photon entering into
the phenol solution because, at high concentration, a significant amount of UV light may be absorbed by the phenol molecules themselves rather than the catalyst. This also will reduce the catalyst efficiency. In the case of ZnO-TiO₂, continuing increase in degradation rate even beyond the optimum phenol concentration for ZnO or TiO₂, indicates the availability of more reaction sites. Hence the formation/availability of electrons and hole may be more which can react with even more molecules of the substrate in this case. This is possible due to the Interparticle Electron Transfer in the case of ZnO-TiO₂ which increases the availability of electrons and holes, as discussed earlier.

The photo catalytic degradation of organic contaminants over semiconductor oxides generally follows Langmuir- Hinshelwood Kinetic model [130]:

\[-\frac{dC}{dt} = r_0 = k_r C_0 / (1 + K C_0) \] .................................. (33)

where \( r_0 \) is the initial rate of disappearance (mgL⁻¹ min⁻¹) of the pollutant, \( C_0 \) (mgL⁻¹) its initial concentration, \( t \) is the illumination time, \( k_r \) is the reaction rate constant at maximum surface concentration and \( K \) the equilibrium adsorption constant. Eq.33 can be rewritten as

\[1/r_0 = 1/k_r + 1/k_e K \times 1/C_0 \] ........................................ (34)

Plot of \( 1/r_0 \) vs \( 1/C_0 \) yields a straight line in the case of first order kinetics and L-H mechanism. Another more accepted mode of verifying the kinetics is by integrating equation 33, which yields the relation,

\[\ln(C_0/C) + K (C_0-C) = k_r K t \] ........................................ (35)
When $C_0$ is very small, the above equation becomes

$$\ln \left[ \frac{C_0}{C} \right] = -\ln \left[ \frac{C}{C_0} \right] = k_r K_t = k_{\text{app}} t$$

where $k_{\text{app}}$ is the apparent rate constant.

Plotting of $-\ln \left[ \frac{C}{C_0} \right]$ vs time in the concentration range of 10–40 mg/L (Fig. 3.8(b)) shows linear dependence indicating first order kinetics, in the case of ZnO. Beyond this concentration, the rates become independent of the concentration indicating decrease in the order and eventually zero order kinetics.

Fig. 3.8 (b): Kinetics of ZnO mediated photocatalytic degradation of phenol
Fig. 3.8 (c): Kinetics of TiO$_2$ mediated photocatalytic degradation of phenol.

Fig. 3.8 (d): Kinetics of ZnO-TiO$_2$ mediated photocatalytic degradation of phenol.
In the case of TiO₂ and ZnO-TiO₂, the plot is not strictly linear in the concentration range (10-40 mg/L) as seen in Fig. 3.8 (c & d). Hence the kinetics may be different from that in the case of ZnO. This needs more detailed investigation especially due to the IPET and other combination effects of ZnO or TiO₂.

It is clear that, in the case of all three catalysts, the rate increases with increase in initial concentration of the substrate at lower concentration range. The results are consistent with first order kinetics. However, at higher concentrations, in the case of ZnO and TiO₂ the increase in rate slows down, suggesting a reduction in the order of the reaction. In the case of ZnO –TiO₂, the rate continues to increase with concentration at least in the range of our study and hence the variable kinetics is not manifested here. At high substrate concentrations, all the catalytic sites of the semiconductor surface are occupied and concentration is not a constraint for the reaction to proceed. At low concentrations, the number of catalytic sites is not the limiting factor for the degradation rate, which is then proportional to the substrate concentration in accordance with apparent first order kinetics. The generation and migration of photogenerated electron-hole pairs in the semiconductor oxide catalysts and the reaction between photogenerated hole (hydroxyl radical) and organic compounds are the two processes that occur in series. Therefore, each step may become rate determining for the overall process. At lower concentrations, the latter process dominates and therefore the degradation rate increases linearly with the concentration of the organic compound. On the contrary, at higher concentrations, the former will become the governing step and the degradation rate increases
slowly with concentration and even a constant degradation rate may be reached at higher concentration for a given illumination intensity. The effective number of active sites available for phenol adsorption is drastically reduced, once the surface is almost fully occupied and this also contributes to the reduction in rate of degradation at higher substrate concentrations. However, in the case ZnO/TiO₂, the availability of electron and hole will be more compared to ZnO or TiO₂ individually due to IPET and this leads to an increase in the rate of degradation even at relatively higher concentration of the substrate. Decrease in the rate of photocatalytic degradation and hence, in the order of the reaction at higher concentrations of the reactant has been reported earlier also [133,143-150]. With increase in concentration of substrate, more reactant molecules get adsorbed onto the catalyst site, get activated and interact with correspondingly more Reactive Oxygen Species. This will continue until all the surface sites are occupied by the substrate. Thereafter, increase in concentration cannot result in increased surface occupation and the phenol removal becomes independent of its concentration. Complete domination of the surface by the reactant/ intermediates/ products can result in suppression of the generation of surface initiated reactive free radicals which also results in decreased rate.

3.3.5 Effect of pH

Photocatalytic reaction of organic compounds in solution takes place on the particulate surface of the semiconductor. The pH of the reaction medium is known to have a strong influence on UV-induced degradation of organic pollutants. In photolysis, the possibility of bond breakage and its site might be different at different pH due to the
difference in the distribution of molecular charges. The surface charge of semiconductors, the interfacial electron transfer and the photoredox processes occurring in their presence are also affected by pH. Hence, the effect of pH on the photocatalytic degradation of phenol was investigated in the range 3-11, in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$. The pH of the suspension was adjusted initially and was not controlled during irradiation. The results are shown in Fig. 3.9(a).

![Graph showing the effect of pH on the photocatalytic degradation of phenol over ZnO, TiO$_2$ and ZnO-TiO$_2$.](image)

Fig.3.9(a): Effect of pH on the photocatalytic degradation of phenol over ZnO, TiO$_2$ and ZnO-TiO$_2$.

The degradation rate of the pollutant was found to increase with increase in pH initially in presence of all three catalysts. However, the
degradation decreases above pH 5, in the case of ZnO and ZnO-TiO$_2$ and above pH $\approx 6$ in the case of TiO$_2$. The point of zero charge (PZC) of ZnO and TiO$_2$ are about 9.3 and 6.5 respectively. Depending on the pH, the catalyst surface will be either positively charged (for pH<PZC) or negatively charged (for pH> PZC), or remain neutral (for pH = PZC). This characteristic significantly affects the adsorption and desorption properties of the semiconductor. In addition, the chemical characteristic of the pollutants are also influenced by pH.

The optimum pH for efficient degradation of phenol is 5.5-6.0 in all cases. The degradation is less in extreme acidic and alkaline region. With increase in pH from 3 to 6, the degradation of phenol increases. For ZnO-TiO$_2$, the pH effect is quite similar to that of ZnO. Higher degradation efficiency in the acidic range has been reported for phenol using TiO$_2$ as the catalyst [133,151]. At pH < PZC when catalyst surface is positively charged, phenol in its neutral form can get closer to the surface or weakly adsorbed. At pH > PZC, when the ZnO/TiO$_2$/ZnO-TiO$_2$ surface is negatively charged, phenol in its neutral or ionized form will keep away from the surface thereby resulting in reduced degradation. In extremely acidic solutions, photodegradation efficiency is less. In the case of ZnO, it is also because of photocorrosion which is significant at pH less than 4. As expected, the pH effect on ZnO-TiO$_2$ is a combination of the individual effects of ZnO and TiO$_2$. In order to verify the correlation between the extent of adsorption and degradation of phenol on the catalysts at different pH, the effect of pH on the adsorption on respective catalysts is measured. Results are shown in Fig. 3.9(b).
As seen, maximum adsorption is observed in the range 5.5–7.0 and it decreases thereafter in the alkaline range. The results further indicate that the pH dependence of photocatalytic degradation of phenol cannot be fully correlated to the adsorption characteristics even though the trend shows some similarities. In addition to affecting the surface properties of the catalyst, pH also influences direct photolysis of phenol and the reactive •OH radical formation [152]. Alkaline range is expected to favour the formation of more OH radicals from the large quantity of OH ions present which could enhance the degradation significantly. However, this is not reflected in the actual degradation rate possibly due to the poor adsorption.
The effect of pH can be explained at least partially based on the amphoteric behaviour and surface charge of catalyst. The acid-base property of metal oxides can influence their photocatalytic activity significantly. Solution pH influences the ionization state of ZnO surface according to the reactions:

At acidic pH: \[\text{Zn} - \text{OH} + \text{H}^+ \leftrightarrow \text{ZnOH}_2^+ \] ............................ (37)

At alkaline pH: \[\text{Zn} - \text{OH} + \text{OH}^- \leftrightarrow \text{Zn-O}^- + \text{H}_2\text{O} \] ................... (38)

pKa value of phenol is 9.98. In the alkaline pH range, where phenol is expected to be in the ionized form, the adsorption on ZnO will be weaker. Hence, the surface mediated degradation will be less. However, under acidic conditions, phenol which remains mainly in the neutral form can get adsorbed or come closer to the catalyst surface as explained earlier, resulting in its degradation via interaction with bulk hydroxyl radicals produced in the aqueous media. However, the concentration of \text{OH} radicals will be relatively less. In the optimum pH range of 5.5-7, there will be reasonably good proximity of phenol to the surface adsorption and adequate population of \text{OH} radicals which will explain the optimum degradation of phenol.

In the case of TiO$_2$, solution pH influences the ionization state of TiO$_2$ surface according to the reactions:

At acidic pH: \[\text{Ti} - \text{OH} + \text{H}^+ \leftrightarrow \text{Ti-OH}_2^+ \] ............................ (39)

At alkaline pH: \[\text{Ti} - \text{OH} + \text{OH}^- \leftrightarrow \text{Ti-O}^- + \text{H}_2\text{O} \] ................. (40)
At pH < ~7, when the TiO₂ surface is positively charged, phenol which is in neutral form can get closer to the surface or weakly adsorbed. At pH > 7, when the surface is negatively charged, phenol in neutral or ionized form will keep away from the surface. The mechanism of pH effect is same as in the case of ZnO and hence the similarity in the trend. As expected, the pH effect on the ZnO-TiO₂ is more or less similar to that on ZnO. The results clearly indicate that there is no well-defined direct correlation between PZC of the semiconductor oxide catalyst, adsorption and the photocatalytic degradation rate. This is in line with the observation reported by many other workers also [153-158].

3.3.6 Effect of reaction volume

Optimization of reaction volume and hence reactor size is important from the commercial application angle for any process. Hence the effect of reaction volume on the rate of photocatalytic degradation of phenol is investigated and the results are shown in Fig. 3.10(a). It is seen that the % degradation decreased with increasing reaction volume. However, the actual rate of degradation in terms of the number of molecules of phenol degrading increases with volume. The rate of degradation even slows down at higher volume and stabilizes. The rate of degradation with volume of the reaction system is plotted in Fig. 3.10(b). The increasing rate with increase in volume may be attributed to the higher number of phenol molecules in the system which leads to more frequent interaction with surface and the reactive free radicals generated from it. However when the volume exceeds the critical limit, penetration of the light becomes less, light gets scattered and photons reaching the surface of the catalyst will be less. Further the surface also will get saturated with the phenol molecules.
Fig. 3.10 (a): Effect of reaction volume on the photocatalytic degradation of phenol over ZnO, TiO$_2$, and ZnO-TiO$_2$.

Fig. 3.10 (b): Effect of reaction volume on the rate of degradation of phenol.
This results in stabilized or decreased rate of the semiconductor activation and phenol degradation. Hence reaction volume vs reactor geometry and size are important in the design of a photocatalytic system.

3.3.7 Effect of particle size

Particle size is one of the important parameters that influences the photocatalytic efficiency of semiconductors. The inverse relation between particle size of the catalyst and the rate of photocatalytic reactions has been reported in many instances. Decrease in particle size leads to increase in surface area, more surface sites for adsorption of the pollutant and better surface promoted interaction between the reactants resulting in higher conversion in photocatalysis. The effect of particle size in the range 4.5 to 18 µm on the degradation of phenol is investigated and the results are shown in Fig. 3.11. The influence of particle size in this limited range is minimal for ZnO, TiO₂ and ZnO-TiO₂. However, particles in the nano ranges at one end and higher size at the other end can influence the rate of photocatalytic degradation significantly. The effect of particle size, shape, distribution etc of the catalyst on the photocatalytic degradation of trace pollutants in a major field of investigation, especially in identifying optimum characteristic for catalyst particle. That is beyond the scope of the current study and hence not pursued.
3.3.8 Effect of aeration/deaeration

O₂ dissolved in the system/ remaining adsorbed on the catalyst is known to play an important role in the photocatalytic degradation reaction. The O₂ serves as an electron scavenger by trapping electron from the conduction band and preventing recombination [95]. The reduction of O₂ and the adsorption of substrate take place at different locations on the catalyst surface and hence presence of O₂ is not detrimental to the adsorption efficiency. O₂ also contributes to the formation of ROS, stabilization of reactive free radicals, intermediates, mineralization and direct photocatalytic reaction.
The effect of dissolved air/oxygen on the photocatalytic degradation of phenol was tested by purging the system with N2 for 1 hr in the presence of each of the three catalysts. The results are as shown in Table 3.1. The degradation rate is inhibited in the system purged with N2. Introduction of air into the system enhances the degradation because of increased supply of O2 including the replacement. This shows that dissolved oxygen has a significant role in the photocatalytic degradation of phenol. The main role of O2 is inhibition of the electron-hole recombination and thus enhancing the formation of ROS. O2 also enhances the amount of H2O2 and in turn OH radicals which enhances the efficiency of photocatalysis.

\[(O_2)_{ads} + e^- \rightarrow O_2^- \] .................................................. (41)
\[H_2O \rightarrow OH^- + H^+ \] ..................................................... (42)
\[O_2^- + H^+ \rightarrow HOO^- \] .................................................... (43)
\[HOO^- + e^- \rightarrow HO_2^- \] ......................................................... (44)
\[HOO^- + H^+ \rightarrow H_2O_2 \] .................................................. (45)
\[H_2O_2 + e^- \rightarrow OH^- + OH^- \] ................................................ (46)
\[H_2O + h^+ \rightarrow H^+ + OH^- \] ................................................. (47)

Table 3.1: Effect of aeration/deaeration of the reaction system on the photocatalytic degradation of phenol.
[Catalyst]: [0.1g/L]; [phenol]: 40 mg/L; pH: 5.5-6; Reaction Volume: 50 ml; Irradiation Time: 120 min.

<table>
<thead>
<tr>
<th>Purging gas</th>
<th>Percentage Degradation of phenol on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnO</td>
</tr>
<tr>
<td>None</td>
<td>55</td>
</tr>
<tr>
<td>N₂</td>
<td>23</td>
</tr>
<tr>
<td>Air</td>
<td>65</td>
</tr>
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3.4 Probable mechanism of the photocatalytic degradation of phenol in presence of semiconductor

The primary step in heterogeneous photocatalytic process is the adsorption of the organic substrate on the surface sites. Activation of semiconductor is achieved through the absorption of a photon (hv) from UV irradiation source. When the energy is sufficient, depending on the band gap of the semiconductor, promotion of an electron from the valence band to the conduction band takes place. Thus electron hole pairs are created. The electrons are taken up by adsorbed O₂ resulting in the formation of superoxide radical anion and ultimately OH radicals through a series of reactions. The radicals and other reactive oxygen species initiated by the activated catalyst surface interact with the substrate (phenol). The basic mechanism of the photocatalytic degradation can be schematically represented in different forms. One of the simplest schematic presentations is given in Fig. 3.12.

![Fig.3.12: A simplified mechanism for photocatalytic process on a semiconductor [34.](image)]
Various steps involved in the process are as follows.

\[ \text{hv} \quad \text{Semiconductor} \rightarrow e_{cb}^- + h_{vb}^+ \text{ (48)} \]

The excited electron-hole pairs generated can recombine, either in the bulk or at the surface releasing the input energy as heat, with no chemical effect. However, if the electrons and holes migrate to the surface of the semiconductor without recombination, they can participate in various oxidation and reduction reactions with adsorbed species such as water, oxygen, and other organic or inorganic species. These processes, i.e., oxidation of a suitable electron donor adsorbed on the surface by photogenerated hole and reduction of electron acceptor adsorbed on the surface by photogenerated electron, constitute the basic mechanisms of photocatalytic water/air remediation and photocatalytic hydrogen production, respectively.

The reaction steps involved in the process after the photoexcitation as in reaction (48) as given in reaction (41 - 47).

The positive hole can oxidize pollutants directly. However, in most cases it reacts with water (i.e., hydroxide ion, OH\(^-\)) to produce the hydroxyl radical (\(^{\cdot}\)OH), which is a very powerful oxidant with oxidation potential of 2.8 V vs NHE. \(^{\cdot}\)OH rapidly attacks pollutants at the surface as well as in solution and mineralizes them into CO\(_2\), H\(_2\)O etc [40, 41].

Hydroxyl radical (OH\(^-\)) and superoxide radical anion (O\(_2^\cdot\)) are the primary oxidizing species in the photocatalytic oxidation processes. They cause the degradation of the organic (RH) pollutants by oxidation via successive attack by OH radicals:
RH + ‘OH → R’ + H₂O ............................................... (49)
R + h⁺ → R⁺ → degradation products  ....................... (50)

Various intermediates have been reported during the photocatalytic degradation of phenol [159]. These include catechol (CC), hydroquinone (HQ) and p-benzoquinone (BQ), pyrogallol (PG), Hydroxy benzoquinone (HBQ) etc. (see Fig. 3.13) However, in the present case, only three intermediates could be identified. They are CC, HQ and BQ. Preliminary studies showed that intermediates also get degraded faster. Hence they go undetected.

Various reactive oxygen species formed as above will interact with phenol as shown in Fig. 3.13. Ultimately all these intermediates also get degraded and eventually mineralize into CO₂ and H₂O as shown below:
Reactive oxygen species + phenol → Intermediates → H₂O + CO₂ ......(51)

Fig.3.13: Various reactive oxygen species formed in the reaction system.
The moderately enhanced activity of ZnO-TiO$_2$ compared to individual ZnO and TiO$_2$ may be explained partially based on the improved adsorption and the concept of interparticulate electron transfer [153]. In ZnO/TiO$_2$ composites, the electron is transferred from the conduction band of ZnO to the conduction band of TiO$_2$ under illumination and, conversely, the hole is transferred from the valence band of TiO$_2$ to the valence band of ZnO, decreasing the pairs’ recombination rate. This charge separation effectively increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates. When both semiconductors in coupled system are illuminated simultaneously and their valence and conduction bands are suitably disposed, both electron and hole transfer can occur. This will influence the efficacy of degradation mediated by the oxides. The concept of IPET is illustrated with the help of various semiconductor pairs in Fig. 3.14 [160-165].
Fig. 3.14: (A). Energy diagram illustrating the coupling of various semiconductors (SCs) in which vectorial electron transfer occurs from light-activated SC to the non-activated SC.

(B): Diagram depicting the coupling of various SCs in which vectorial displacement of electrons and holes is possible.
3.5 Formation and decomposition of H$_2$O$_2$

H$_2$O$_2$ is detected as a by-product during the photocatalytic degradation of phenol in presence of ZnO, TiO$_2$ as well as ZnO-TiO$_2$. However, its concentration does not increase with time or with the degradation of phenol. In fact, the concentration of H$_2$O$_2$ is increasing and decreasing periodically indicating concurrent formation and decomposition. The variation in the concentration of H$_2$O$_2$ with time in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$ is given in Fig.3.15.

![Fig.3.15: Fate of H$_2$O$_2$ formed during the photocatalytic degradation of phenol.](image-url)
The concentration of H$_2$O$_2$ does not have any correlation with the degradation/mineralization of phenol. The degradation of phenol continues to increase with time. However the concentration of H$_2$O$_2$ is fluctuating with time in the case of ZnO and TiO$_2$. In the case of ZnO-TiO$_2$ it remains almost stable after initial increase. The concentration of H$_2$O$_2$ formed in situ increases initially, reaches a maximum, starts decreasing, reaches a minimum and then it starts rising again. This periodic increase and decrease in the concentration of H$_2$O$_2$ (oscillation) indicates its concurrent formation and decomposition. In the case of ZnO-TiO$_2$, after moderate increase in the beginning, the rates of formation and decomposition of H$_2$O$_2$ balance and hence its concentration remains steady. When the rate of formation dominates, the concentration increases and reaches a maximum. From this point onwards, the decomposition dominates and the concentration of H$_2$O$_2$ decreases.

Hydrogen peroxide can be formed either through the reduction of O$_2$ by electron in the conduction band (e$^{-}_{cb}$) or by the oxidation of H$_2$O by holes in the valence band (h$^{+}_{vb}$). H$_2$O$_2$ is formed from both H$_2$O and OH$^{-}$ ions by surface oxidation caused by the photogenerated holes and also by the disproportionation of the superoxide radical anion. Various steps involved in the formation of H$_2$O$_2$ can be as follows:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{H}^{+} + e^{-} &\rightarrow \cdot \text{OH} + \text{H}_2\text{O} \quad \text{(52)} \\
\text{H}_2\text{O}_2 + \cdot \text{OH} &\rightarrow \text{HO}_2^{+} + \text{H}_2\text{O} \quad \text{(53)} \\
\text{H}_2\text{O}_2 + 2\text{h}^{+}_{\text{vb}} &\rightarrow \text{O}_2 + 2\text{H}^{+} \quad \text{(54)} \\
\text{H}_2\text{O}_2 + \cdot \text{OH}/\text{h}^{+}_{\text{vb}} &\rightarrow \text{HO}_2^{+} + \text{H}_2\text{O}/\text{H}^{+} \quad \text{(55)}
\end{align*}
\]
Semiconductor Oxides Mediated Photocatalytic Degradation of Phenol in Water

\[ \text{HO}_2^- + \cdot \text{OH}/h^+_{VB} \rightarrow \text{O}_2 + \text{H}_2\text{O}/\text{H}^+ \] .................................. (56)

\[ \text{H}_2\text{O}_2 \rightarrow 2\cdot \text{OH} \] .......................................................... (57)

\[ \text{H}_2\text{O}_2 \text{ (bulk)} \rightarrow \text{H}_2\text{O}_2 \text{ (ad)} \] ........................................ (58)

\[ \text{HO}_2^- \text{ (ad)} + \text{HO}_2^- \text{ (ad)} \rightarrow \text{H}_2\text{O}_2 \text{ (ad)} + \text{O}_2 \text{ (ad)} \] .............. (59)

\[ \text{O}_2\text{(ad)} + e^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- \text{ (ad)} + \text{HO}^- \text{ (ad)} \] .................... (60)

\[ \text{HO}_2^- \text{ (ad)} + e^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \text{ (ad)} \] ........................................ (61)

\[ \text{H}_2\text{O}_2 \text{ (ad)} + e^- \rightarrow \text{OH} \text{ (ad)} + \text{HO}^- \text{ (ad)} \] ....................... (62)

\[ \text{HO}_2^- \text{ (ad)} \rightarrow \text{HO}_2^- \text{ (bulk)} \] ............................................... (63)

\[ \text{HO}^- \text{ (ad)} \rightarrow \text{HO}^- \text{ (bulk)} \] ................................................... (64)

\[ \text{H}_2\text{O}_2 \text{ (ad)} \rightarrow \text{H}_2\text{O}_2 \text{ (bulk)} \] ............................................... (65)

\[ \text{O}_2 \text{ (ad)} \rightarrow \text{O}_2 \text{ (bulk, gas)} \] ................................................. (66)

ad: adsorbed

However, concurrent decomposition of \( \text{H}_2\text{O}_2 \) is caused by reduction by the conduction band electron [94, 95] and the reactions are as follows:

\[ \text{O}_2 + 2 e^-_{cb} + 2\text{H}^+_{aq} \rightarrow \text{H}_2\text{O}_2 \] .................................................. (67)

\[ \text{H}_2\text{O}_2 + \text{H}^+ + e^- \rightarrow \cdot \text{OH} + \text{H}_2\text{O} \] ........................................ (68)

\[ \text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \] ............................................. (69)

\[ \text{H}_2\text{O}_2 + 2h^+_{VB} \rightarrow \text{O}_2 + 2\text{H}^+ \] ............................................... (70)

\[ \text{H}_2\text{O}_2 + .\cdot \text{OH}/h^+_{VB} \rightarrow \text{HO}_2^- + \text{H}_2\text{O}/\text{H}^+ \] .............................. (71)
Chapter 3

The radicals as well as H₂O₂ can accelerate the degradation of phenol. The radicals can also interact with H₂O₂ resulting in decomposition and formation of even more free radicals. So the concentration of H₂O₂ increases initially and decreases thereafter showing that the H₂O₂ formed are undergoing simultaneous decomposition.

The acceleration of the degradation of phenol by H₂O₂ and/or the free radicals resulting from it, is tested by adding H₂O₂ at the beginning of the experiment and evaluating the phenol at various intervals. The results are shown in Table 3.2.

Table 3.2: Effect of added H₂O₂ on the Photocatalytic degradation of phenol under UV.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Degradation of phenol without added H₂O₂ at the end of</th>
<th>% Degradation of phenol with added H₂O₂ at the end of</th>
<th>% Enhancement by added H₂O₂ at the end of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 min</td>
<td>60 min</td>
<td>90 min</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.8</td>
<td>14.6</td>
<td>26.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>7.0</td>
<td>17.5</td>
<td>33.2</td>
</tr>
<tr>
<td>ZnO-TiO₂</td>
<td>9.2</td>
<td>18.3</td>
<td>36.6</td>
</tr>
</tbody>
</table>

H₂O₂ enhances the degradation of phenol significantly in the beginning. This enhancement is due to the faster decomposition of added H₂O₂ in presence of UV producing maximum OH radicals which can degrade phenol. However, the decomposition of H₂O₂ to water and oxygen also occurs in parallel which restricts the continued availability of
the oxidizing species for phenol degradation resulting in a decrease in degradation rate at a later stage. Further, it must be noted that even in those experiments without externally added \( \text{H}_2\text{O}_2 \), the \( \text{H}_2\text{O}_2 \) formed in-situ has been already accelerating the reaction rate [166].

The effect of initially added \( \text{H}_2\text{O}_2 \) is not that prominent in the later stages of the reaction. \( \text{H}_2\text{O}_2 \) accelerates the degradation in all cases following a fairly uniform pattern. The degree of enhancement varies in the case of the three catalysts with maximum in the case of \( \text{TiO}_2 \) and the minimum in the case of \( \text{ZnO-TiO}_2 \). However, the trend remains the same showing that the mechanism of degradation of phenol as well as the formation and decomposition of \( \text{H}_2\text{O}_2 \) is more or less the same in all three cases.

### 3.6 Effect of anions

In industrial waste waters, phenols and other pollutants are present along with many other natural/man-made organic and inorganic materials which can affect the photocatalytic degradation. In this context, the effect of few added salts/anions like \( \text{Cl}^- \), \( \text{I}^- \), \( \text{SO}_4^{2-} \), \( \text{F}^- \), \( \text{CO}_3^{2-} \), \( \text{NO}_3^- \), \( \text{Br}^- \) and \( \text{PO}_4^{3-} \) on the rate of photocatalytic degradation was investigated. Fig.3.16 (a, b and c) show the results obtained with different anions in the case of \( \text{ZnO}, \text{TiO}_2 \) and \( \text{ZnO-TiO}_2 \) as catalysts.
Chapter 3

Fig. 3.16(a): Effect of anions on the photocatalytic degradation of phenol over ZnO.

Fig. 3.16(b): Effect of anions on the photocatalytic degradation of phenol over TiO₂.
Fig. 3.16(c): Effect of anions on the photocatalytic degradation of phenol over ZnO-TiO$_2$.

In the case of ZnO catalyst, Cl$^-$, I$^-$, SO$_4^{2-}$, Br$^-$ and PO$_4^{3-}$ inhibit the reaction in the order I$^-$ > Cl$^-$ > PO$_4^{3-}$ > SO$_4^{2-}$ > Br$^-$ while CO$_3^{2-}$ and NO$_3^-$ do not have much effect on the reaction rate. The effect of F$^-$ also can be treated as insignificant or slight inhibition. In the case of TiO$_2$ catalyst, Cl$^-$, I$^-$, SO$_4^{2-}$, NO$_3^-$, Br$^-$, PO$_4^{3-}$ inhibit the reaction in the order Br$^-$ > Cl$^-$ > SO$_4^{2-}$ > PO$_4^{3-}$ > NO$_3^-$ > I$^-$ while CO$_3^{2-}$ and F$^-$ do not have any significant effect. The effect of NO$_3^-$ and I$^-$ can be considered as negligible within the limits of experimental error.

In the case of ZnO-TiO$_2$, inhibition decreases in the order Br$^-$ > Cl$^-$ > SO$_4^{2-}$ > PO$_4^{3-}$ > I$^-$ while NO$_3^-$, CO$_3^{2-}$ and F$^-$ have no effect. Thus the anions have more or less similar effect on ZnO-TiO$_2$ as in the case of
TiO$_2$. Though the effect is not quite identical in the case of these three catalysts, a general trend is obvious. Analysis of the effect of each of the anion on each catalyst requires in depth study on the role of a number of parameters which is beyond the scope of the current study. Such investigation are in progress in our laboratory at present.

The inhibition by anions can be broadly explained by the general mechanism of photocatalysis. The experiments were conducted at pH 5.5, which is below the PZC of ZnO and TiO$_2$. Hence, the semiconductor particles will be carrying positive charge. Consequently, the anions can be strongly adsorbed onto these particles through ionic forces. The reaction of surface holes with these undesirable ions leads to a decrease in the formation of hydroxyl radicals, resulting in low photocatalytic efficiency.

The inhibition by halide ion I$^-$, Cl$^-$ and Br$^-$, though in varying degrees, may be explained as follows:

The halide ions(X$^-$) scavenge the photoproduced holes and the hydroxyl radicals more effectively as in reaction 72-75.

$$X^- + h^+ \rightarrow X^* \quad \text{...................................................... (72)}$$

$$X^- + X^* \rightarrow X^- \quad \text{...................................................... (73)}$$

$$HO^* + X^- \rightarrow HOX^- \quad \text{...................................................... (74)}$$

$$HOX^- + H^+ \rightarrow X^* + H_2O \quad \text{...................................................... (75)}$$

Scavenging the highly reactive hydroxyl radical, results in their decreased role in the degradation of phenol.
In this respect, the relatively lower inhibition by F$^-$ is surprising. However, instances of similar behaviour by F$^-$ in TiO$_2$ photocatalysis have been reported earlier also. Calsa and Pelizetti [155] explained this phenomenon as given below:

The holes formed during the irradiation of the semiconductors responsible for the photocatalytic degradation can be either in the bulk or trapped on the surface. When F$^-$ ions get strongly adsorbed on the surface, the holes are bound and effectively $^-$OH is replaced from the surface. The reactive $^-$OH interacts with the hole in the bulk resulting in enhanced formation of $^+$OH radicals. These $^+$OH radicals can compensate at least partially for the surface sites lost to F$^-$. The redox potential of the coupled F/F$^-$ is 3.6 eV which makes fluoride stable against valence band holes. Hence the negligible effect of fluoride may be due to the bulk homogeneous OH reaction and the direct electron transfer from the organic compound to the relatively more abundant valence band hole. However, this may not be the complete picture and the effect may be more complex and not amenable to simple explanation.

The deactivation and decrease in the concentration of hydroxyl radicals caused by SO$_4^{2-}$ can be explained as follows:

$$\text{SO}_4^{2-} + \cdot \text{OH} \rightarrow \text{SO}_4^{\cdot-} + \text{OH}^- \hspace{1cm} (76)$$

The sulphate radical ions (SO$_4^{\cdot-}$) can react with water to produce more sulphate ions

$$\text{SO}_4^{\cdot-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} + \text{H}^+ \hspace{1cm} (77)$$
SO₄⁻ is also a strong oxidant which can contribute to the degradation of phenol

SO₄⁻ + Phenol → Mineralisation products  .................. (78)

Of the two reactions (76) and (77), the latter will be more facile resulting in regeneration of SO₄²⁻ which will again lead to trapping of hydroxyl radicals as in (76). Further, the anion gets adsorbed on to the surface of the catalyst thereby denying access to the phenol molecule. Decreased access to surface sites and reduced the availability of active OH radicals result in a decreased degradation in presence of sulphate ions. However, this is partially compensated by the parallel regeneration of OH radicals as in reaction (77). Hence, the inhibition is relatively less in the case of SO₄²⁻.

PO₄³⁻ ions are well known to get strongly adsorbed on the surface of semiconductor oxide. They compete with phenol for the adsorption sites on the surface of the photocatalyst. They can also scavenge OH to form the corresponding anion radicals PO₄³⁻, which leads to a decrease in the oxidation process. However, in this case also, simple competitive adsorption and blocking of surface sites may not be sufficient to explain the role of PO₄³⁻. The strong inhibition by PO₄³⁻, reported in the case of many photocatalytic processes is absent in the current instance, probably because the bulk process is also equally dominating. In the case of NO₃⁻ and CO₃²⁻ the effect on the degradation of phenol is negligible. Both the anions are known to be weakly adsorbed on the surface of semiconductors [155-159,167-169]. They are also not known as strong OH radical scavengers. Hence, these anions do not influence the semiconductor
catalysed photodegradation of phenol, at least under the conditions of the current study.

3.7 Conclusions

The photocatalytic degradation of phenol pollutant in water in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$ catalyst is investigated. The efficiency of the catalysts is in the order ZnO-TiO$_2$ > TiO$_2$ > ZnO. H$_2$O$_2$ formed during the photocatalytic degradation undergoes simultaneous formation and decomposition resulting in oscillation in its concentration. Major intermediates of phenol degradation are catechol, hydroquinone and p-benzoquinone. Ultimately they also degrade fully resulting in the complete mineralization of the pollutant into relatively harmless end products, i.e., CO$_2$ and H$_2$O. Possible mechanism for the photocatalytic degradation of phenol, formation and decomposition of H$_2$O$_2$ and the enhanced activity of coupled ZnO-TiO$_2$ are discussed. Various anions likely to be present in water influences the photocatalytic degradation differently. However, there is no general trend indicating the complexity of the effect of anions in photocatalysis.
4.1 Introduction

As explained in Chapter 3, the photocatalytic degradation needs high power ultraviolet light to induce excitation of the semiconductor. This restricts the application of photocatalysis for the treatment of turbid/opaque waste waters of low transparency. The photocatalytic activity cannot be enhanced by increasing catalyst dosage beyond a limit due to ineffective light penetration and its scattering. The substrate itself can absorb part of the light in many cases reducing the radiation available for catalyst activation. In order to overcome these drawbacks, ultrasound was examined instead of ultraviolet light as the irradiation source for the activation of various semiconductor oxides for the degradation of organic pollutants. This method was reported to yield positive result for the treatment of different types of pollutants in water. However, the