Ultrasound assisted semiconductor mediated catalytic degradation of organic pollutants in water: Comparative efficacy of ZnO, TiO$_2$ and ZnO-TiO$_2$

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Abstract

Sonocatalytic degradation of organic pollutants in water is investigated using ZnO, TiO$_2$ and combination of ZnO and TiO$_2$ (ZnO-TiO$_2$) as catalysts, with phenol as the test substrate. The efficacy of the catalysts is in the order ZnO-TiO$_2$ > ZnO > TiO$_2$. The degradation in presence of ZnO-TiO$_2$ is more than the sum of the degradation achieved in presence of the individual oxides under identical conditions, thereby demonstrating a synergistic effect. The ratio of the components in the mixed oxide is optimized. The kinetics of the degradation as well as the influence of various parameters such as catalyst loading, concentration of the pollutant and pH on the degradation efficiency is evaluated. Maximum degradation is observed in the acidic pH for all catalysts. H$_2$O$_2$ is formed in the reaction and it undergoes simultaneous decomposition resulting in periodic increase and decrease in its concentration. This observation of the phenomenon of oscillation in the concentration of H$_2$O$_2$ is the first of its kind in sonocatalytic systems. A mechanism for the degradation of phenol is proposed based on the observations as well as the concurrent formation and decomposition of H$_2$O$_2$.

Keywords: Zinc oxide, titanium dioxide, sonocatalysis, phenol, hydrogen peroxide.

Introduction

Advanced Oxidation Processes (AOP) involving Ultraviolet light, Fenton reagents, Ozone, Ultrasound etc have been tested individually as well as in combination, in the presence and absence of catalysts for the treatment of wastewater containing pesticides, phenols, chlorophenols, dyes and other pollutants [1-5]. The mechanism in all these cases involves the formation of active ·OH radicals which mineralize the pollutants into carbon dioxide, phosphates, sulphates etc.

Recently, Ultrasonic (US) irradiation mediated by suitable catalysts (sonocatalysis) has been receiving special attention as an environment - friendly technique for the treatment of hazardous organic pollutants in wastewater[6]. However the degradation rate is slow compared to other established methods. Investigations aimed at enhancing the efficiency of US promoted decontamination of water are in progress in many laboratories. These include testing a variety of catalysts with different physico-chemical characteristics, modification of reactor design and reaction conditions, combining US with other AOP techniques etc[6-9]. Coupling US with Ultraviolet (UV) irradiation enhances the efficiency of semiconductor mediated degradation of aqueous pollutants synergistically[6,7,10,11].

In liquids US produces cavitation which consists of nucleation, growth and collapse of bubbles. The collapse of the bubbles results in localized supercritical condition such as high temperature, pressure, electrical discharges and plasma effects[10]. The temperature of the gaseous contents of a collapsing cavity can reach approximately 5500^{0}C and that of the liquid immediately surrounding the cavity reaches up to 2100^{0}C. The localized pressure is estimated to be around 500 atmospheres resulting in the formation of transient supercritical water[12]. The cavities are thus capable of functioning like high energy micro reactors. The consequence of these extreme conditions is the cleavage of dissolved oxygen molecules and water molecules into radicals such as H·, OH· and O· which will react with each other as well as with H$_2$O and O$_2$ during the rapid cooling phase giving HO$_2$· and H$_2$O$_2$. In this highly reactive nuclear environment, organic pollutants can be decomposed and inorganic pollutants can be oxidised or reduced. This phenomenon is being explored in the emerging field of sonocatalysis for the removal of water pollutants.

Most of the studies on the sonocatalytic degradation of water pollutants are made using TiO$_2$ catalyst, mainly due to its wide availability, stability, non-toxicity and reactivity. Another similar semiconductor oxide ZnO has received relatively less attention possibly due to its corrosive nature under extreme pH conditions. At the same time ZnO is reported to be more efficient than TiO$_2$ for the visible light induced photocatalytic degradation of organic pollutants because the former can absorb a larger fraction of solar spectrum compared to the latter [13,14]. Earlier studies in our laboratory showed that ZnO is very efficient as a sono catalyst and sonophotocatalyst for the degradation of trace pollutants in water[15]. Comparative study of the catalytic

activity of nano-sized TiO_2, ZnO and composite TiO_2/ZnO powders for the sonocatalytic degradation of dyestuffs showed that the composite powder is more effective[16]. Similarly Tb_7O_{12}/TiO_2 composite was reported to perform better as sonocatalyst compared to the individual oxides for the degradation of amaranth[17]. In spite of the multitude of research papers on the sonocatalytic activity of TiO_2 and its modified forms, not many reports are available on the use of ZnO or coupled ZnO-TiO_2 as sonocatalysts for the removal of water pollutants. In this paper we report the comparative assessment of the sonocatalytic activity of ZnO, TiO_2 and ZnO-TiO_2 for the removal of trace amounts of phenol in water and the factors influencing their performance.

Material and Methods

ZnO and TiO_2 used in the study were supplied by Merck India Limited. In both cases the particles were approximately spherical and nonporous with over 99% purity. The surface areas of TiO_2 and ZnO, as determined by the BET method are 15 and 12 m^2/g respectively. ZnO-TiO_2 catalysts were prepared by physically mixing respective components in required weight ratios and thoroughly mixing for 30 minutes using mechanical shaker. Phenol AnalaR Grade (99.5% purity) from Qualigen (India) was used as such without further purification. Doubly distilled water was used in all the experiments. All other chemicals were of AnalaR Grade or equivalent. The average particle size of both ZnO and TiO_2 was 10 μm, unless mentioned otherwise.

The experiments were performed using aqueous solutions of phenol of the desired concentration. Specified quantity of the catalyst is suspended in the solution. In the case of US irradiation experiments, sonication was sufficient to ensure adequate mixing of the suspension. Additional mechanical mixing did not make any notable consistent difference in the US reaction rate. The reactor was a cylindrical Pyrex vessel of 250 ml capacity. In the case of sonocatalytic experiments, ultrasonic bath was used as the source of US. The ultrasonic bath operated at 40 kHz and power of 100 W. Water from the sonicator was continuously replaced by circulation from a thermostat maintained at the required temperature. Unless otherwise mentioned, the reaction temperature was maintained at 27 $\pm$ 1^{0}C. The position of the reactor in the ultrasonic bath was always kept the same. At periodic intervals samples were drawn, the suspended catalyst particles were removed by centrifugation and the concentration of phenol left behind was analyzed by Spectrophotometry at 500 nm. H_2O_2 is determined by standard iodometry. Degradation and mineralization were identified by the evolution of CO_2. Adsorption studies were performed as follows[18]:

A fixed amount (0.1 g) of the catalyst was introduced to 100 ml of phenol solution of required concentration in a 250 ml beaker and the pH was adjusted as required. The suspension was agitated continuously at constant temperature of 27 $\pm$ 1^{0}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 supernatant was determined colorimetrically. The adsorbate uptake was calculated from the relation : $q_e = (C_0 - C_e)V / W$

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 liter, W is the mass of the adsorbent in gram and q_e is the amount adsorbed in mg per gram of the adsorbent.

Results and Discussion

Preliminary investigations on the sonocatalytic degradation of phenol were made using ZnO and TiO_2 catalysts under identical conditions. The results show that ZnO with 14% degradation of phenol is more efficient as sonocatalyst than TiO_2 with 7% degradation in 2 hr time under otherwise identical conditions.

No significant degradation of phenol took place in the absence of US or the catalyst suggesting that both catalyst and sound are essential to effect degradation. Small quantity of phenol degraded under US irradiation even in the absence of the catalyst. This is understandable since sonolysis of water is known to produce free radicals $H^.$ and $OH^.$ (via reaction 1), which are capable of attacking the organic compounds in solution.

$$H_2O \xrightarrow{\quad >>> \quad} H^. + .OH \quad (1) \qquad >>> \text{refers to sonication}$$
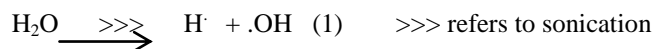
The process is facilitated in a heterogeneous environment such as the presence of ZnO or TiO_2. The presence of the particles helps to break up the microbubbles created by US into smaller ones, thus increasing the number of regions of high temperature and pressure[10]. This leads to increase in the number of OH radicals which will interact with the phenol present in water and oxidise it, resulting in eventual mineralization.

Coupling of ZnO and TiO_2 in the weight ratio 1:1 results in 13.5% phenol degradation which is same as in the case of ZnO of same mass. This is more than the sum of degradation achieved in the presence of individual ZnO and TiO_2 at loadings equivalent to their concentration in the combination, thereby showing synergistic effect. The % degradation varies with the composition of ZnO-TiO_2 with maximum degradation of 14% in presence of ZnO/TiO_2 at 4:6 as shown in figure 1. Hence further studies with the ZnO-TiO_2 combination were carried out using this ratio.

The synergy index can be calculated from the rate of degradation using the following equation: Synergy index = $R_{(Z-T)} / (R_Z + R_T)$

where R_Z, R_T and $R_{(Z-T)}$ are sono catalytic degradation rates in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$ respectively. The maximum synergy index thus calculated is approx. 1.30 for ZnO concentration of 10% (by mass) in the coupled ZnO-TiO$_2$. With increase in the concentration of ZnO in the couple, the synergy index drops slowly. Beyond 40% concentration of ZnO, the couple behaves more like pure ZnO as a sonocatalyst.

The effect of various parameters on the efficiency of the catalysts is investigated in detail in order to optimize the conditions of degradation of phenol in presence of each of them.

Effect of catalyst dosage: The effect of catalyst dosage on the sonocatalytic degradation of phenol is studied at different loadings of ZnO, TiO$_2$ and ZnO-TiO$_2$. The results are plotted in figure 2.
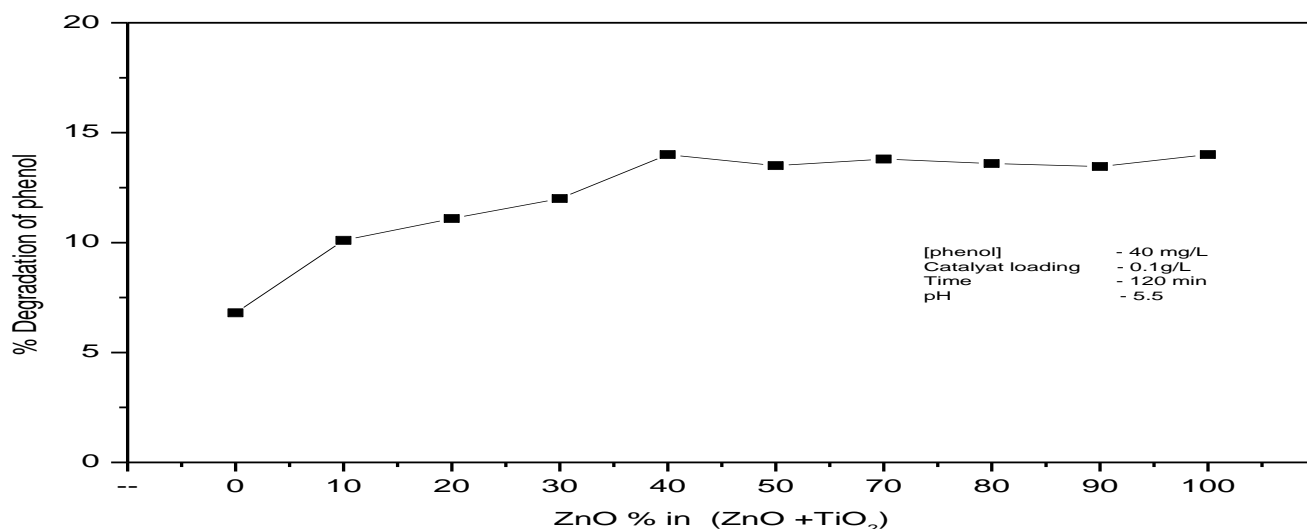

Figure-1
Effect of ZnO/TiO2 ratio on the sonocatalytic activity

Figure-2
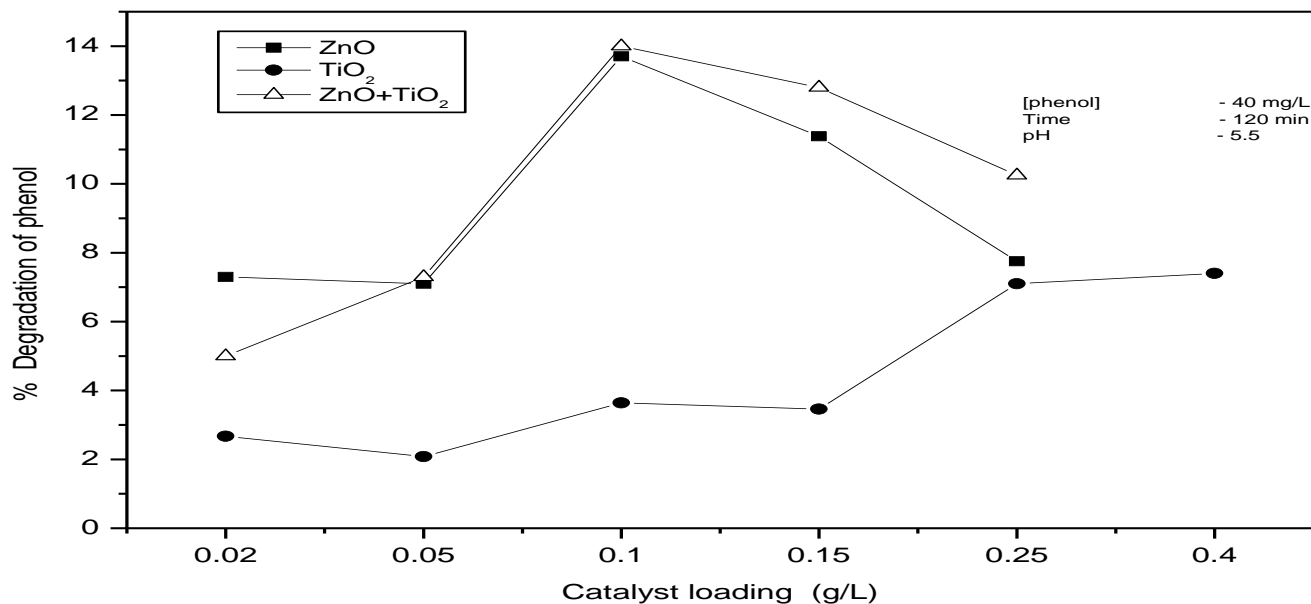**Effect of catalyst dosage on the sonocatalytic activity of ZnO, TiO$_2$ and ZnO+TiO$_2$**

In all three cases the degradation increases with increase in catalyst loading and reaches an optimum range. Beyond this optimum, the degradation slows down and thereafter remains more or less steady or even decreases. The enhanced degradation efficiency with increase in the dosage is probably due to increased number of catalytic sites, higher production of OH radicals and more effective interaction with the substrate. It is known that the addition of particles of appropriate amount and size into the liquid system results in increase in the acoustic noise and a rise in temperature in the irradiated liquid[19]. Introduction of more catalyst particles in the solution provide more nucleation sites for cavitation bubbles at their surface. This will result in decrease in the cavitation thresholds responsible for the increase in the number of bubbles when the liquid is irradiated by US. The increase in the number of cavitation bubbles increases the pyrolysis of water and the sonocatalytic degradation of phenol. Any further increase in catalyst concentration beyond the optimum will only result in the particles coming too close to each other or aggregating thereby limiting the number of active sites on the surface. Higher concentration of the suspended particles may also disturb the transmission of ultrasound in water medium. Hence no further increase in the degradation of the pollutant is observed beyond the optimum dosage. However the number of particles alone or the effect of ultrasound on them is not the only factor leading to increased degradation with increase in catalyst dosage, as seen in the difference in the optimum amount of ZnO , TiO_2 or $ZnO-TiO_2$ with comparable particle size and surface area. Surface and bulk interactions of the reactant molecules play an important role in the sonocatalytic degradation of organics in suspended systems.

The increase in the degradation of phenol with increase in catalyst dosage as observed here is inconsistent with the report that adsorption of the pollutant molecules on the surface may protect them from ultrasonic degradation [20]. The adsorption of phenol on the catalysts is determined at the optimum degradation dosages and the values are 24, 16 and 19 mg/g of the catalyst for TiO_2, ZnO and $ZnO-TiO_2$ respectively. TiO_2 is a better adsorber compared to the other two catalysts. However, the sonocatalytic activity is less compared to ZnO thereby confirming that adsorption is not the major factor in sonocatalysis. At the same time increase in the degradation rate with increase in catalyst loading, as observed in the current study shows that adsorption does not inhibit the degradation altogether. Adsorption helps the surface initiated degradation on the one hand and protects at least partly, the adsorbed species from cavitation effects. At the same time cavitation is known to alter the adsorption/desorption/degradation rates [21].

The current study shows that ZnO is more efficient than TiO_2 for the degradation of phenol. Appropriate combination of $ZnO -TiO_2$ is having the same activity as ZnO. This also shows that the effect of particles is not limited to cavitation

or its consequences alone. Irradiation of aqueous solution by ultrasound is known to produce ultraviolet light by sonoluminescence[22]. Since ZnO is known to be a better harvester of light[14], the higher sonocatalytic activity can be at least partly attributed to the photocatalysis occurring during US irradiation. The presence of suspended particles lead to better propagation of the ultrasonic wave in the suspended medium resulting in the production of cavitation bubbles and emission of light throughout the reactor. This light can activate ZnO leading to the production of OH radicals which can either react with phenol and degrade it or recombine to produce H_2O_2. Higher adsorption of the pollutant on the surface of the catalysts is known to retard the absorption of light resulting in lower degradation. At the same time lower adsorption can result in decreased reaction rate, prolonged degradation time and even incomplete degradation. Hence reasonable degree of adsorption combined with good absorption of light resulting from sonoluminescence lead to good sonocatalytic activity of semiconductor oxides. The higher activity of $ZnO-TiO_2$ indicates that the better adsorption capability of TiO_2 and the light absorption capability of ZnO can be suitably exploited to achieve maximum degradation of the pollutant in water by sonocatalysis.

H_2O_2 formation and decomposition: Formation of H_2O_2 is observed in the case of sonocatalytic and photocatalytic degradation of phenol in presence of ZnO, TiO_2 and $ZnO-TiO_2$. Hydrogen peroxide is produced even in the absence of phenol indicating the formation of free radicals OH and HO_2 in liquid water by US/UV. The results are shown in figures 3 and 4.

The results indicate that H_2O_2 formation is more in presence of UV than US in the case of ZnO and $ZnO-TiO_2$. In the case of TiO_2, the H_2O_2 formed is more in presence of US compared to UV, at least in the initial stages. In the case of US, the concentration of H_2O_2 is less in the presence of phenol probably because some of the ˙OH radicals formed may be reacting with phenol before they could recombine to produce H_2O_2. Also in this case, thermal decomposition of H_2O_2 to water and oxygen rather than to reactive radical species may be occurring[23]. In the case of TiO_2 the difference in H_2O_2 concentration in the reaction system, between in the presence and absence of phenol is not significant. In this case, the degradation of phenol is also less. The concentration of H_2O_2 is increasing and decreasing periodically showing that it is undergoing simultaneous formation and decomposition. At the same time, the degradation of phenol continues without break, though the rate of degradation slows down with time.

The decomposition and consequent decrease in the concentration of H_2O_2 is more evident even in the initial stages in the case of TiO_2. It is also pertinent to note that the maxima and minima attained in the case of respective

catalysts remain more or less in the same range, irrespective of the number of crests and valleys. This suggests that there is some kind of an equilibrium concentration for H_2O_2 in each system, at which the rate of decomposition and formation balances each other. The maximum concentration of H_2O_2 reached is different for different catalysts indicating that it is dependent on the catalyst. Similar oscillatory behavior in the concentration of H_2O_2 during photocatalysis [24] and sonophotocatalysis[15] has been reported earlier. It is known[25] that H_2O_2 decomposes and produces OH radicals during, sono, photo and sonophotocatalysis. These radicals can accelerate the degradation of phenol. This is tested by adding H_2O_2 in the beginning of the experiments. The results are shown in table 1.
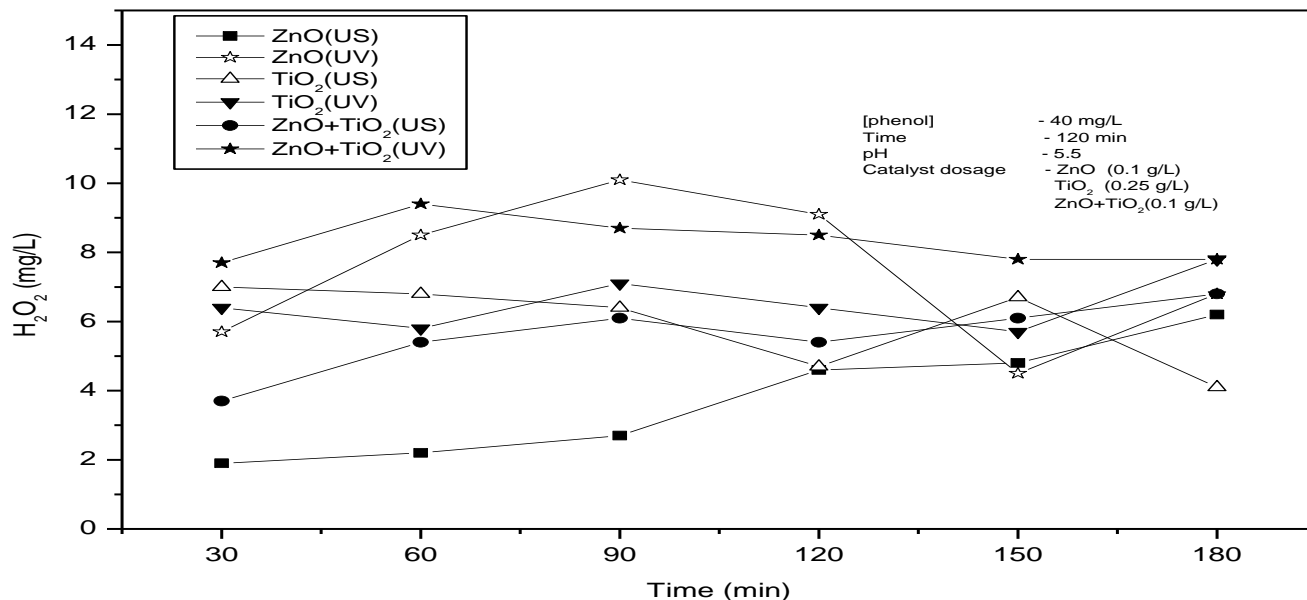

Figure-3
Oscillation in the concentration of H_2O_2 in the presence of phenol under sono and photo catalytic condition on various catalysts
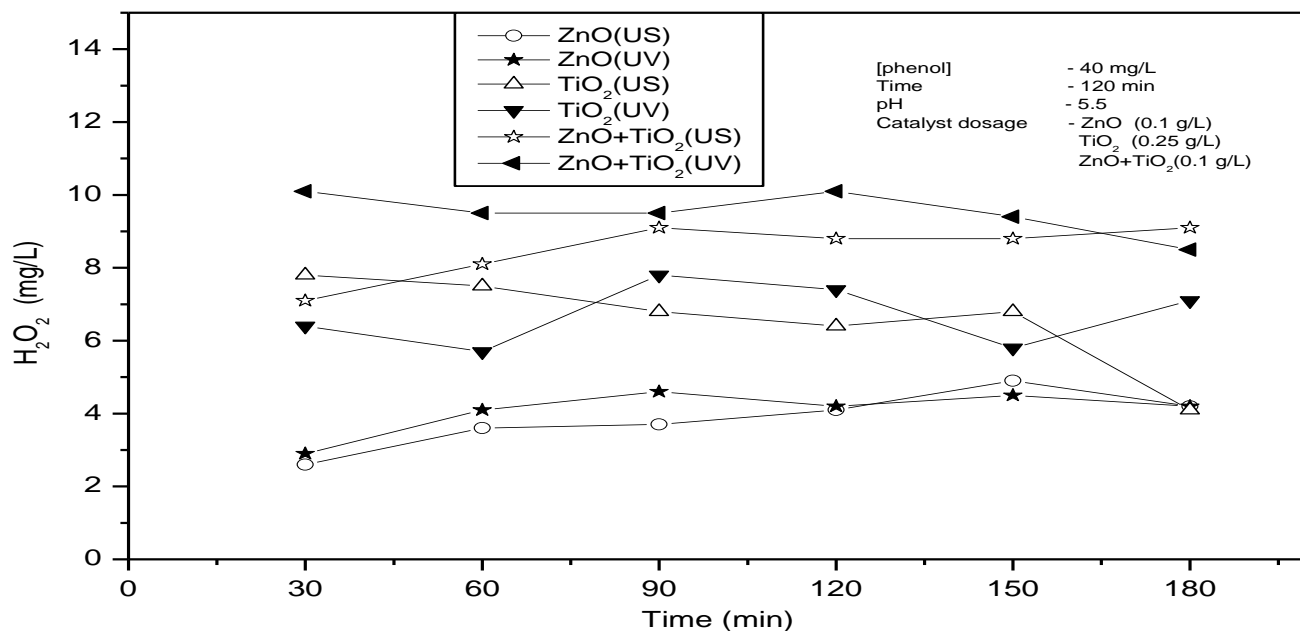

Figure-4
Oscillation in the concentration of H_2O_2 in the absence of phenol under sono and photo catalytic condition on various catalysts

Table 1
Effect of added H_2O_2 on the degradation of phenol under US, UV and (US + UV)

[Catalyst]: 0.1g/L   pH: 5.5   Reaction Volume: 50 ml   [Phenol]: 40 mg/L

Reaction Condition	% Degradation of phenol without added H_2O_2			% Degradation of phenol with added H_2O_2			% enhancement by added H_2O_2		
	30 min	60 min	90 min	30 min	60 min	90 min	30 min	60 min	90 min
US (ZnO)	1.1	6.0	9.5	3.0	7.1	11.2	172.7	18.3	17.9
UV (ZnO)	7.0	17.5	33.2	14.3	31.2	44.7	104.3	78.3	34.6
US (TiO_2)	0.8	3.7	5.2	1.8	4.7	5.8	125.0	27.0	11.5
UV (TiO_2)	5.8	14.6	26.3	10.5	24.8	34.6	81.0	70.0	31.6
US (ZnO-TiO_2)	1.1	6.2	10.1	2.7	7.4	11.4	145.5	19.4	12.9
UV (ZnO-TiO_2)	9.2	18.3	36.6	16.1	29.5	45.8	75.0	61.2	25.1

H_2O_2 enhances the degradation of phenol significantly in the beginning. However this high rate of enhancement is not sustained later on. This can be explained as follows:

In the beginning, added H_2O_2 decomposes faster in presence of UV and US producing maximum OH radicals which can degrade phenol. However, the decomposition of H_2O_2 to water and oxygen also occurs in parallel which restricts the continued availability of the oxidizing species for phenol degradation. Further, even in those experiments without externally added H_2O_2, the H_2O_2 formed insitu will be accelerating the reaction rate. Hence the effect of initially added H_2O_2 is not that prominent in the later stages of the reaction. The decrease in the enhancement of degradation with time is relatively less in the case of UV. Here the decomposition of H_2O_2 is occurring slowly thereby making the OH radicals available for degradation reaction for extended period. The thermal decomposition of H_2O_2 into inactive H_2O and O_2 also is lower in the case of UV irradiation compared to US.

H_2O_2 accelerates the degradation in all cases following a fairly uniform pattern. The enhancement effect is comparable in the case of ZnO and ZnO-TiO_2. This shows that in the case of the coupled catalyst, the mechanism of degradation of phenol as well as the formation and decomposition of H_2O_2 is more or less dictated by ZnO since it has higher sono and photocatalytic activity compared to TiO_2.

Concentration Effect: The effect of concentration of phenol on the rate of degradation is investigated. The results are plotted in figure 5.

In the case of ZnO, TiO_2 as well as ZnO-TiO_2 the rate increases linearly with increase in concentration at lower concentration range of 10-40 mg/L. At higher concentrations, the rate slows down as the concentration increases. Thus the degradation follows first order kinetics at lower concentration which changes to lower order at higher concentration. Decrease in the rate of degradation and hence

in the order of the reaction at higher concentration of the reactant has been reported in the case of photocatalysis[26,27], sonocatalysis[28] as well as sonophotocatalysis[15]. In the present study the kinetics observed in the case of all three catalysts is similar indicating that the mechanism of degradation may be the same. However, the change of reaction order takes place at slightly lower concentration ranges in the case of TiO_2 showing the role of surface characteristics and adsorption on the rate of reaction.

Sonocatalytic reactions occur at the surface, in the bulk as well as at the interface of the cavitation bubble. At the surface of the collapsed bubble, the concentration of the OH radicals is relatively high. At low concentration, when the amount of phenol at the surface or in the bulk is low, a considerable part of the OH radicals will recombine yielding H_2O_2. Only about 10% of the OH radicals generated in the bubble can diffuse into the bulk solution[29]. These factors result in lower degradation of phenol. With increase in concentration, the probability of interaction of OH radicals with phenol increases on the surface as well as in the bulk resulting in increased rate of degradation. The degradation rate slows down and reaches almost a constant level when the concentration of phenol on the catalyst surface as well as at the bubble surface reach a saturation limit during the persistence of the bubble. This is in agreement with earlier findings[30].

The general mechanism of sonocatalytic degradation in aqueous medium involves the formation of OH radicals and their attack on the organic substrate. This can also explain the decrease in the recombination of OH radicals resulting in lower concentration of H_2O_2 at higher concentration of phenol[31]. At higher concentration of the substrate, the surface is fully covered as a result of which it cannot effectively absorb the light produced by ultrasound, resulting in decreases photocatalytic effect and eventual stabilization. Also at higher concentrations, the phenol molecules can act as mutual screens thereby preventing effective interaction of all molecules with the ultrasound [32].

Effect of pH: The pH of the reaction medium is known to have strong influence on US or UV-induced degradation of organic pollutants. In photolysis, the possibility of bond breakage and the site might be different at different pH due to difference in the distribution of molecular charges. In sonocatalytic reaction, pH can alter the distribution of the pollutants in the bulk region, on the surface and at the site of the cavity collapse. The surface charge of semiconductors and the interfacial electron transfer and the photoredox processes occurring in their presence are also affected by pH. Hence the effect of pH on sonocatalytic degradation of phenol was investigated in the range 3-11. The pH of the suspension was adjusted initially and it was not controlled during the irradiation. The results are presented in figure 6.
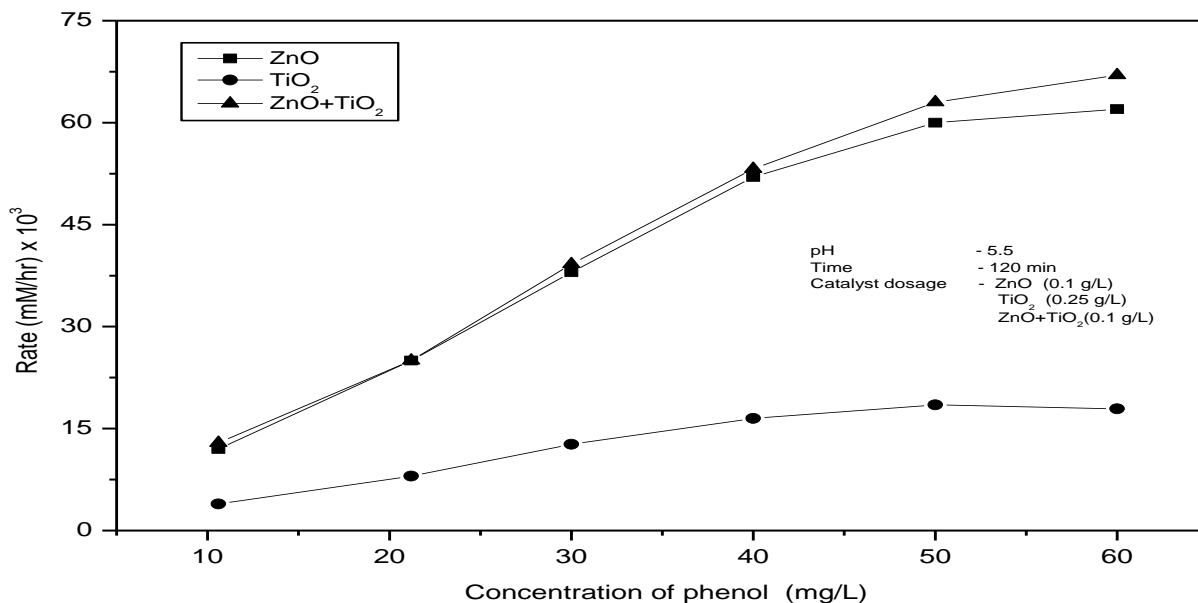

Figure-5
Effect of concentration of phenol on the intial rate of sonocatalytic degradation on various catalysts
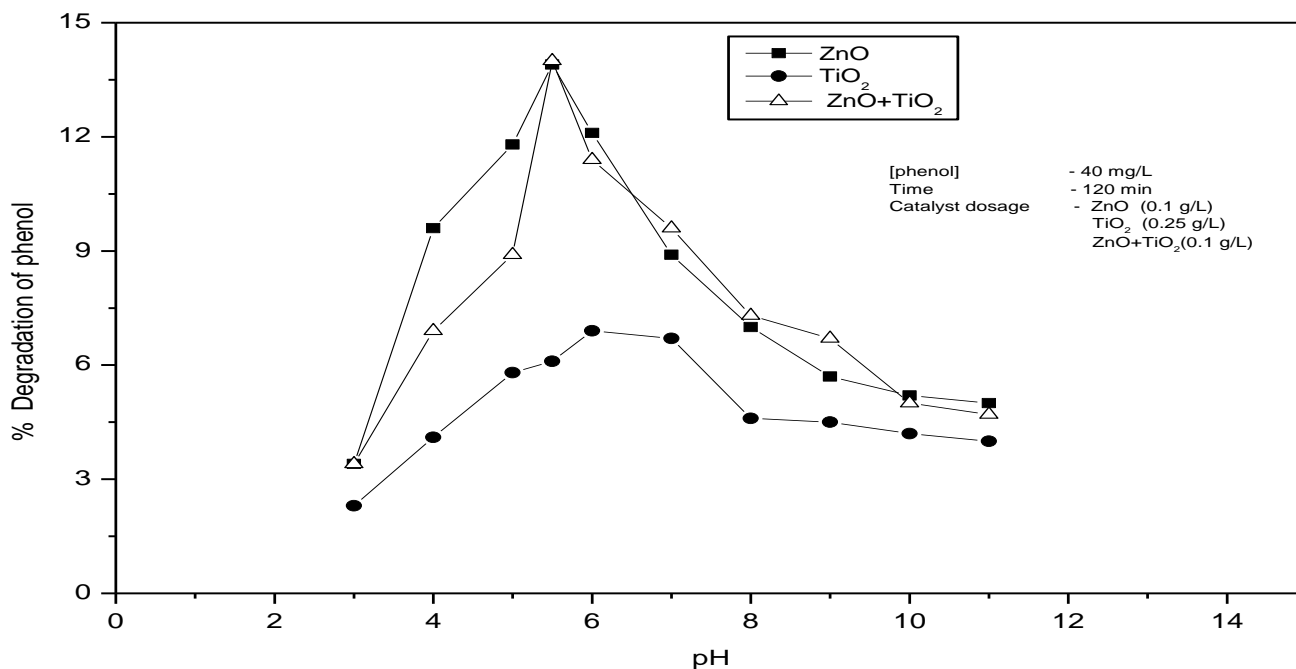

Figure-6
Effect of pH on the sonocatalytic degradation of phenol on various catalysts

The degradation is more efficient in the acidic region than in the alkaline region in the case of the three catalysts tested here. In the case of ZnO, maximum degradation is observed in the acidic pH range of 4-6, which peaks at pH 5.5. In the case of TiO_2 also similar trend follows with the maximum at pH 6. For ZnO-TiO_2, the pH effect is quite similar to that of ZnO as expected. The optimum pH in all these cases is 5.5-6. Higher degradation efficiency in the acidic range has been reported by other authors also [33-35] with different types of phenol using TiO_2 as the catalyst. The steep fall in degradation rate below pH 4 in the case of ZnO and ZnO-TiO_2 can be attributed to the corrosion of ZnO under acidic conditions.

The pH of the reaction medium has significant effect on the surface properties of semiconductor oxide particles, including the surface charge, size of the aggregation and the band edge position[36]. Hence pH can affect the adsorption – desorption characteristics of the surface of the catalyst. However, in the case of sonocatalysis, adsorption is not the only factor leading to the degradation for reasons explained earlier.

The acid-base property of metal oxides can influence their photocatalytic activity significantly. The Point of Zero Charge (PZC) of ZnO and TiO_2 are 9.3 and 6.8 approximately[14]. This means that the catalyst surface is positively charged when the pH is lower than respective PZC value and negatively charged when the pH is higher. Solution pH influences the ionization state of ZnO surface according to the reaction:

$$---Zn-OH + H^+ \leftrightarrow ZnOH_2^+ \qquad (2)$$
$$--Zn-OH + OH^- \leftrightarrow Zn-O^- + H_2O \qquad (3)$$
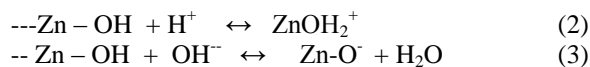
In the alkaline pH range, where phenol is expected to be in the ionized form, the adsorption on ZnO will be weaker. Hence the surface mediated degradation will be less. However under acidic conditions, phenol which remains mainly in the neutral form can get adsorbed or come closer to the catalyst surface, resulting in its degradation via active surface species or bulk hydroxyl radicals produced in the aqueous media. Further, the presence of more protons can facilitate the formation of reactive OH radicals from the available OH ions. Significant enhancement in the degradation can also be attributed to the effect of US in reducing the distance between the substrate molecule and the surface of the catalyst particles. This is not feasible in the alkaline range where repulsion between like charges of the substrate and the catalyst particles is much greater [16].

Similarly in the case of TiO_2, solution pH influences the ionization state of TiO_2 surface according to the reaction[11]

$$\geq Ti-OH + H^+ \leftrightarrow \geq Ti-OH_2^+ \qquad (4)$$
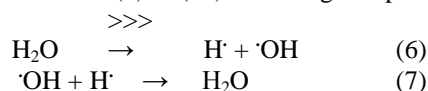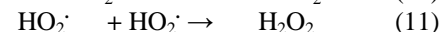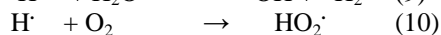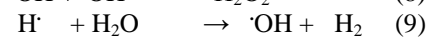$$\geq Ti-OH + OH^- \leftrightarrow \geq Ti-O^- + H_2O \qquad (5)$$
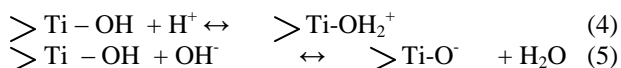
At pH less than ~7, when the TiO_2 surface is positively charged, phenol which is in neutral form can get closer to the surface or weakly adsorbed. At pH > 7, when the surface is negatively charged, phenol in neutral or ionized form will keep away from the surface. In the case of ZnO, weak adsorption or al least phenol coming closer to the surface is possible upto pH 9. Hence the surface promoted sonocatalytic degradation is more in the case of ZnO than TiO_2. As expected, the pH effect on the ZnO-TiO_2 is more or less similar to that on ZnO. The results clearly indicate that there is no well defined correlation between PZC of the semiconductor oxide catalyst and the sonocatalytic degradation rate.

Possible mechanism: Sonocatalytic degradation is generally explained based on sonoluminescence and hot spot theory. Ultrasonic irradiation results in the formation of light of a comparatively wide wavelength range of 200 -500 nm. Those lights with wavelength below 375 nm can excite the semiconductor catalyst and generate highly active OH radicals on the surface. Thus the basic mechanism is partly that of photocatalysis. At the same time the more complex phenomenon of formation of hotspots upon implosion of some bubbles on the catalyst surface also leads to the formation of electron-hole pairs and excess OH radicals[14]. Since the formation of electron-hole pairs is the first step in both photocatalysis and sonocatalysis, the efficiency of the process depends on the ability to prevent their recombination. This is achieved to some extent by combining the semiconductor oxides ZnO and TiO_2 which is one of the reasons for the observed synergy here. Under ultrasonic irradiation, a series of thermal and photochemical reactions take place on the surface of composite TiO_2/ZnO particles[16]. Because of the difference in adsorption capacity, the TiO_2 part is inclined to the hole oxidation and ZnO tends towards radical oxidation. The electron transport in the TiO_2/ZnO prevents the electron – hole recombination and increases the sonocatalytic activity. Because the TiO_2 and ZnO possesses similar energy band gap (3.2 eV) the electrons can transfer easily from TiO_2 to ZnO through the crystal interface between the two which results in complete separation of electrons and holes. Such electron transport through the crystal interface of composite oxides has been reported earlier also[17].

The overall mechanism of H_2O_2 formation and the decomposition of phenol under sonocatalytic conditions can be explained as follows:
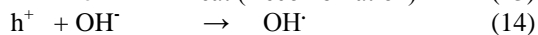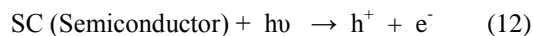
Acoustic cavitation produces highly reactive primary radicals such as OH and H as in reaction (6). Recombination and a number of other reactions occur within the bubble as in reactions (7) to (11) following this primary radical generation

$$H_2O \xrightarrow{>>>} H^. + {}^.OH \qquad (6)$$
$${}^.OH + H^. \rightarrow H_2O \qquad (7)$$

$\cdot OH + \cdot OH \rightarrow H_2O_2$ (8)
$H\cdot + H_2O \rightarrow \cdot OH + H_2$ (9)
$H\cdot + O_2 \rightarrow HO_2\cdot$ (10)
$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2$ (11)

OH radical is a nonselective oxidant with a high redox potential (2.8 eV) which is able to oxidise most organic pollutants [37].

Similarly the photocatalytic reaction initiated by ultrasound can be represented as follows[38]:
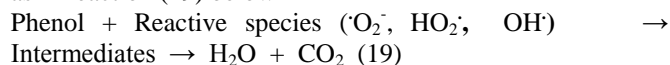
$SC \text{ (Semiconductor)} + h\upsilon \rightarrow h^+ + e^-$ (12)
$h^+ + e^- \rightarrow \text{Heat (Recombination)}$ (13)
$h^+ + OH^- \rightarrow OH\cdot$ (14)
$h^+ + H_2O \rightarrow OH\cdot + H^+$ (15)

Scavenging of conduction band electrons
$e^- + O_2 \rightarrow \cdot O_2^-$ (16)

Formation of multiple peroxide species
$H^+ + \cdot O_2^- \rightarrow HO_2\cdot$ (17)
$HO_2\cdot + e^- + H^+ \rightarrow H_2O_2$ (18)
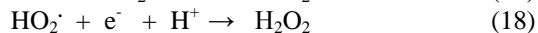
Various reactive species produced as above react with phenol as in reaction (19) below

Phenol + Reactive species $(\cdot O_2^-, HO_2\cdot, OH\cdot) \rightarrow$ Intermediates $\rightarrow H_2O + CO_2$ (19)

Once sufficient concentration of H_2O_2 is reached, its decomposition also sets in as follows:

$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O$ (20)
$HO_2\cdot + \cdot OH \rightarrow H_2O + O_2$ (21)
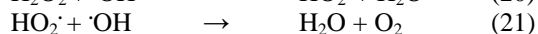
H_2O_2 can also lead to reduction in charge recombination by taking up the electron

$SC (e^-) + H_2O_2 \rightarrow SC + HO\cdot + OH^-$ (22)

H_2O_2 can also produce OH radicals directly or reaction with superoxide anion

$H_2O_2 \xrightarrow{h\upsilon} 2 \cdot OH$ (23)
$H_2O_2 + \cdot O_2^- \rightarrow 2 \cdot OH + O_2$ (24)

Conclusion

The sonocatalytic activity of ZnO, TiO_2 and ZnO-TiO_2 for the degradation of phenol pollutant in water is investigated. The efficacy of the catalysts for the degradation is in the order ZnO-TiO_2 > ZnO > TiO_2. At lower concentrations of ZnO, the percentage degradation in the presence of coupled ZnO-TiO_2 is more than the sum of the degradation achieved in the presence of individual oxides under identical conditions, implying a synergistic effect. The catalyst loading, irradiation time, initial pH and concentration of the substrate have profound effect on the rate of degradation. H_2O_2 formed during the degradation of phenol undergoes simultaneous decomposition as well. After initial accumulation upto certain concentration, decomposition of H_2O_2 also sets in resulting in oscillation in its concentration. Possible mechanism for the sonocatalytic degradation of phenol, formation and decomposition of H_2O_2 and the enhanced activity of coupled ZnO-TiO_2 is discussed.

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