5.1 Introduction

As highlighted in Chapters 3 and 4, semiconductor mediated photocatalysis and sonocatalysis respectively have been investigated extensively as viable techniques for the removal of organic and inorganic pollutants from aqueous streams. The techniques have been proven moderately effective for the oxidative destruction of recalcitrant organic compounds such as dyes [61], pesticides [192], phenols [62,193,194] and the reduction of several heavy metals [195]. However, sonocatalysis has still not gained acceptance as an adequately efficient and effective stand-alone technology for the commercial level decontamination of wastewater. Photocatalysis is used at commercial level for limited application though its potential as an efficient waste management technology is still not fully explored. Attempts to enhance the efficiency
of photocatalytic treatment of wastewater by adding $\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, $\text{Fe}^{3+}$, cations, anions, dyes, etc. to the reaction system and modification of catalyst characteristics by doping, supporting and coating have also been reported [196-200].

Recently, combination of sonocatalysis and photocatalysis (sonophotocatalysis) has been receiving attention as a promising technique for the treatment of hazardous organic pollutants in wastewater [171, 177, 201]. It has been reported that combining US with Ultraviolet (UV) irradiation enhances the efficiency of semiconductor mediated degradation of aqueous pollutants synergistically [56, 59, 112, 140, 202-207, 208]. Similarity in the mechanism of photocatalytic and sonocatalytic reactions, enhances the advantage of combining these techniques. However, very few reports are available on this combination, which have been summarized in a recent review [208]. The degradation of phenol under photo and sonocatalytic conditions in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$ is investigated and reported in previous chapters. Hence, a detailed study is undertaken on the degradation of trace amounts of phenol contaminant in water under simultaneous presence of US and UV irradiation in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$. The photo and sonocatalytic degradation data from chapters 3 and 4 respectively are compared with the results in this chapter, wherever relevant.
5.2 Experimental Details

5.2.1 Materials

Materials used for the studies in this chapter are as described in Chapters 3 and 4.

5.2.2 Equipment Used

The Mercury Vapor lamp for UV light and the Ultrasonic bath for US are the same as described in Chapters 3 and 4, section 3.2.4 and 4.2.2. respectively. Rest of the equipments used for this experiments are also described in Chapters 3 and 4.

5.2.3 Experiments and Analytical Methods

The experiments were performed using aqueous solutions of phenol of desired concentration. Specified quantity of the catalyst was suspended in the solution. The reaction set up was a combination of those used in Chapters 3 and 4. The reactors were same as those used in photocatalysis. They were placed in an ultrasonic bath in which water from a thermostat at the required temperature was circulated. Unless otherwise mentioned, the reaction temperature was maintained at 29±1 °C. The position of the reactor in the ultrasonic bath was always kept the same. A high intensity UV lamp (400 W medium pressure mercury vapor quartz lamp) mounted above was used as the UV irradiation source. The ultrasonic bath was operated at a frequency of 40 kHz and a power of 100 W unless indicated otherwise. Rest of the experimental procedure, sampling and analysis methods etc were the same as described in Chapters 3 and 4. Typical reactor set up is shown in Fig. 5.1.
5.3 Results and Discussion

Preliminary investigations on the sonophotocatalytic degradation of phenol were made using ZnO, TiO$_2$ and ZnO-TiO$_2$ catalysts under identical conditions. The results are presented in Fig. 5.2.

![Fig.5.1: A schematic diagram of the sonophotocatalytic experimental set up.](image)

![Fig.5.2: Comparison Sonophotocatalytic activities of ZnO, TiO$_2$ and ZnO-TiO$_2$.](image)
The results show that ZnO-TiO$_2$ combination [1:1] with 89.0% degradation of phenol is the most efficient closely followed by ZnO with 85% degradation. The percentage degradation in presence of TiO$_2$ is ~63.1% and is hence the least active of the three.

It was already demonstrated in Chapters 3 and 4 that catalyst and light or catalyst and sound are essential to effect significant degradation. The results in Fig. 5.3 show that the presence of the semiconductor catalyst in combination with light and sound (sonophotocatalysis) enhances the degradation of phenol significantly. The degradation under (UV + US) irradiation is more than the sum of degradation under individual UV and US irradiation, thereby showing a synergistic effect. The synergy can be explained at least partially based on the effects of microstreaming and increased mass transport associated with the interaction of US with solid matter. Microstreaming provides in situ regeneration of the catalyst surface as the cavitation near the solid surface causes a jet of fluid directed onto the particle [82]. Thus the blockage of active adsorption sites on the catalyst can be partially cleared. US also increases the mass transfer on the solid–liquid interface [82,181,198] leading to the generation of more ROS, enhanced adsorption and faster degradation.
The synergy index under sonophotocatalysis irradiation is calculated from the rates of degradation under different conditions using the following equation:

\[
\text{Synergy Index (US+UV)} = \frac{R_{US+UV}}{R_{US} + R_{UV}} \tag{126}
\]

where \( R_{US} \), \( R_{UV} \) and \( R_{US+UV} \) are sono, photo and sonophoto catalytic degradation rates respectively. The synergy index thus calculated is 1.12 for ZnO-TiO\(_2\), 1.25 for ZnO and 1.12 for TiO\(_2\).

The results further showed that just as in the case of sonocatalysis, ZnO is more efficient for the sonophotocatalytic degradation of phenol compared to TiO\(_2\) under identical conditions. This implies that the effect
of the combination of US and UV on respective catalyst, is not much different from that of individual US or UV [56, 59].

The effect of ZnO-TiO\textsubscript{2} ratio in the combination catalyst on the degradation is verified and the results are presented in Fig. 5.4. Maximum degradation of \( \approx 90\% \) is seen in presence of ZnO-TiO\textsubscript{2} in the ratio 4:6. Pure TiO\textsubscript{2} powder (ZnO/TiO\textsubscript{2} = 0:1) gives the lowest degradation of 73 \% of phenol under UV+US irradiation. The degradation increases slowly with increase in ZnO, reaches an optimum, then decreases slightly and stabilizes. The optimum ZnO/TiO\textsubscript{2} ratio is same as in the case of US or UV irradiation, once again confirming that there is not much mechanistic difference in the effect of UV+US combination other than synergy in the combined effect.

![Fig. 5.4: Effect of percentage of ZnO in ZnO-TiO\textsubscript{2} composite on the sonophotocatalytic activity.](image-url)
Summary of the effect of ZnO content in ZnO-TiO$_2$ on US, UV and US+UV degradation of phenol is shown in Table 5.1.

**Table 5.1: Effect of percentage of ZnO in ZnO-TiO$_2$ on US, UV and US+UV.**

[Phenol]: 40 mg/L; pH: 5.5; Reaction Volume: 50 mL; Irradiation time: 120 min

<table>
<thead>
<tr>
<th>% ZnO in ZnO-TiO$_2$</th>
<th>US</th>
<th>UV</th>
<th>US+UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.8</td>
<td>64.7</td>
<td>73.0</td>
</tr>
<tr>
<td>10</td>
<td>10.1</td>
<td>63.7</td>
<td>74.3</td>
</tr>
<tr>
<td>20</td>
<td>11.0</td>
<td>63.4</td>
<td>74.9</td>
</tr>
<tr>
<td>30</td>
<td>12.0</td>
<td>65.7</td>
<td>77.8</td>
</tr>
<tr>
<td>40</td>
<td>14.0</td>
<td>68.1</td>
<td>90.0</td>
</tr>
<tr>
<td>50</td>
<td>13.5</td>
<td>65.4</td>
<td>88.3</td>
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<td>13.1</td>
<td>64.1</td>
<td>87.9</td>
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<td>70</td>
<td>13.8</td>
<td>63.4</td>
<td>86.1</td>
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<td>80</td>
<td>13.6</td>
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<td>85.7</td>
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<tr>
<td>90</td>
<td>13.4</td>
<td>60.1</td>
<td>85.0</td>
</tr>
<tr>
<td>100</td>
<td>14.0</td>
<td>57.4</td>
<td>85.0</td>
</tr>
</tbody>
</table>

5.3.1 Effect of Catalyst loading

It is necessary to determine the optimum catalyst dosage in order to avoid the use of excess catalyst, and to design appropriate reactor system. The sonophotocatalytic degradation of phenol is studied at different loadings of ZnO, TiO$_2$ and ZnO-TiO$_2$ (4:6) keeping all the other parameters identical. The results plotted in Fig. 5.5 show that in all three cases when the catalyst loading is increased from 0.02 to 0.50 g/L, the phenol degradation increases initially. This is followed by a slow and steady decrease at higher loadings. The optimum loading is 0.1 g/L in the case of ZnO and ZnO-TiO$_2$ and 0.25 g/L in the case of TiO$_2$. The maximum degradation attained in sonophotocatalysis is significantly higher than that in the case of photocatalysis and sonocatalysis for all catalyst loadings, thereby...
suggesting that the catalyst as well as the source of irradiation is important for the efficiency of degradation. This is also evident from the nearly identical synergy index value for all the catalysts even though the actual degradation efficiency is more in the case of ZnO-TiO₂. The decrease in degradation with increase in catalyst loading beyond a particular maximum is more pronounced in sonocatalysis and sonophotocatalysis when compared to photocatalysis. However, the optimum loading and the trend remain fairly the same suggesting that US induced increase in rate of photocatalysis is resulting at least partly from the increase in light absorbed by the reaction system. This leads to a higher concentration of active species. At higher catalyst loading when filtering and/or scattering of light becomes important, the amount of photo produced active species does not increase anymore and the synergy between photocatalysis and sonocatalysis also remains almost constant or even decreases. This is understood from the observation that efficiency of photocatalysis which is determined by the processes occurring at the semiconductor-water interface also starts decreasing at around the same catalyst dosage as in the case of sonophotocatalysis. In the case of TiO₂, the optimum catalyst loading is higher compared to ZnO and ZnO-TiO₂. At higher catalyst loadings; the aggregation of particles is one factor responsible for the decrease in rate. Sonication helps to deaggregate the particles which will be more efficient in the case of TiO₂. This will result in the availability of more active light absorbing and adsorbing sites for longer periods.

The optimum catalyst loading will also depend on the size, shape and geometry of the reaction assembly. Hence, for each reactor configuration, the optimization has to be done separately.
Comparison of the optimum catalyst loading under sono, photo and sonophotocatalysis in the case of ZnO, TiO$_2$ and ZnO-TiO$_2$ is tabulated in Table 5.2. In the case of ZnO the optimum is 0.10 g/L for sono, photo as well as sonophotocatalysis. However, in the case of TiO$_2$ the optimum dosage for sono and sonophotocatalysis is 0.25g/L while for photocatalysis, it is 0.1g/L. In the case of ZnO-TiO$_2$ the optimum loading is same as in the case of ZnO i.e., 0.1g/L for sono, photo and sonophotocatalysis. This clearly show that ZnO plays a major role in the sono or photocatalytic behaviour of ZnO-TiO$_2$. The higher optimum dosage in the case of TiO$_2$ as well as its higher photoactivity indicates that it is capable of absorbing more of UV light compared to ZnO.
Table 5.2: Effect of catalyst loading on the US, UV and US+UV induced degradation of phenol in presence of ZnO, TiO₂ and ZnO-TiO₂.

[Phenol]: 40 mg/L; pH: 5.5; Reaction Volume: 50 mL; Irradiation time: 120 min

<table>
<thead>
<tr>
<th>Catalyst loading (g/L)</th>
<th>Percentage Degradation of phenol on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnO</td>
</tr>
<tr>
<td></td>
<td>US</td>
</tr>
<tr>
<td>0.02</td>
<td>7.3</td>
</tr>
<tr>
<td>0.05</td>
<td>7.1</td>
</tr>
<tr>
<td>0.07</td>
<td>10.2</td>
</tr>
<tr>
<td>0.1</td>
<td>13.7</td>
</tr>
<tr>
<td>0.15</td>
<td>11.3</td>
</tr>
<tr>
<td>0.2</td>
<td>10.2</td>
</tr>
<tr>
<td>0.25</td>
<td>7.7</td>
</tr>
<tr>
<td>0.3</td>
<td>7.0</td>
</tr>
<tr>
<td>0.35</td>
<td>6.1</td>
</tr>
<tr>
<td>0.4</td>
<td>6.2</td>
</tr>
<tr>
<td>0.45</td>
<td>6.2</td>
</tr>
<tr>
<td>0.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>

5.3.2 Effect of concentration

The effect of initial concentration of phenol in the range of 10-60 mg/L on the sonophotocatalytic degradation was investigated in presence of ZnO, TiO₂ and ZnO –TiO₂. The results are plotted in Fig. 5.6(a). As in the case of sonocatalysis and photocatalysis, sonophotocatalysis also appears to follow pseudo-first order kinetics. At higher concentrations, the rate slows down as the concentration increases. The first order kinetics of the reaction is confirmed by the logarithmic plot given in Fig. 5.6(b-d). In the case of all three catalysts, the reaction follows similar kinetics, indicating that the mechanism of degradation may be the same. The linear plot of -ln C/C₀ versus time shows that the reaction obeys first order kinetics at
lower concentrations of 10-30 mg/L in the case of ZnO, TiO$_2$ and ZnO - TiO$_2$. Above this concentration, the order decrease, the decrease being steeper above 40 mg/L which is in line with the observations in most sono and photocatalytic processes [130,198-201].

Davydov et al., [113] reported zero order kinetics in the sonophotocatalytic degradation of salicylic acid on TiO$_2$. However, the authors worked in the low conversion regime only. In the present case also, the shift from zero to first order takes place only at higher conversion ranges. The first order kinetics at lower concentrations and higher conversion ranges is understandable from both photocatalytic and sonocatalytic angles. In photocatalysis, with increase in concentration, more reactant molecules get adsorbed onto the catalyst site, get activated and interact with correspondingly more OH radicals. This will continue until all the surface sites are occupied. Thereafter, increase in concentration cannot result in increased surface occupation and the phenol removal becomes independent of concentration. The sonocatalytic degradation takes place in the bulk of the solution where the concentration of OH radicals is relatively smaller [29]. Hence, increase in concentration of phenol can more effectively utilize the otherwise limited OH radicals leading to increased degradation. This will continue until the phenol concentration remains sufficiently high to interact with optimum number of OH radicals.

It is also possible that some of the reaction products and intermediates may remain attached to the surface for relatively longer period towards the later stages of reaction or at higher concentration of the substrate resulting in non-availability of the surface sites for fresh
reactant molecules. Higher substrate concentration can also absorb more photons thereby decreasing the photons available for catalyst activation. In pure photocatalytic systems, complete domination of the surface by the reactant/intermediates/products can result in suppression of the generation of surface initiated OH radicals. However, in presence of US, the saturation of catalyst surface takes place at a relatively later stage due to deaggregation. Further, the reaction can also take place at the cavitation bubble interface where the OH concentration can reach a higher limit. However, the contribution from deaggregation of catalyst particles and the higher OH concentration at the cavitation bubble interface do not influence the kinetics of the degradation of phenol which remains similar under sono, photo and sonophotocatalysis.

![Graph showing the effect of concentration on the sonophotocatalytic degradation of phenol over ZnO, TiO2, and ZnO-TiO2](image-url)

**Fig.5.6(a): Effect of concentration on the sonophotocatalytic degradation of phenol over ZnO, TiO2, and ZnO-TiO2**
Fig. 5.6(b): Kinetics of ZnO mediated sonophotocatalytic degradation of phenol

Fig. 5.6(c): Kinetics of TiO$_2$ mediated sonophotocatalytic degradation of phenol
5.3.3 Effect of pH

pH of the reaction medium has significant effect on the sono and photocatalytic degradation of phenol as seen in earlier chapters. pH affects the properties of semiconductor oxide particles, including the surface charge, size of the aggregation and the band edge position. pH can also affect the adsorption–desorption characteristics of the surface of the catalyst. Hence the effect of pH on sonophotocatalytic degradation of phenol is investigated in the range 3–11. The pH of the suspension was adjusted before irradiation and it was not controlled during the experiment. The results are presented in Fig. 5.7. Maximum degradation is in the acidic region. In the acidic pH range of 4–6, over ≈88% (ZnO-TiO₂), 85% (ZnO) and 74 % (TiO₂) conversion is effected in 2 hr
while it is around 62% (ZnO-TiO₂), 54% (ZnO) and 63 % (TiO₂) in the alkaline range (9-11). The pH for optimum degradation of phenol is 5.5 in presence of ZnO-TiO₂ and ZnO and 6 in presence of TiO₂ as catalysts. This observation is similar to that of Wu et.al [206]. Higher degradation efficiency in the acidic pH has been reported by other authors also [133,150,151,202]. The adsorption of phenol from aqueous solution on ZnO, TiO₂, and ZnO-TiO₂ was studied at different pH values and the results are plotted and described in Chapter 3 Fig. 3.9(b). The effect of pH can be explained at least partially based on the amphoteric behaviour and surface charge of the semiconductors. The acid-base property of metal oxides is known to have considerable influence on their photocatalytic activity, as explained in earlier chapters.

Significant enhancement in the degradation of phenol under sonophotocatalysis 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 [203]. Two important factors responsible for the efficiency of degradation are adsorption of the substrate on the catalyst surface and the reactive OH radical formation. These are affected conversely by the pH resulting in a balancing effect, though to a limited extent. Hence the degradation appears to be stabilized in the alkaline range.

The synergy in the sonophotocatalytic degradation is seen at all pH values. The synergy is more at extreme acidic and alkaline pH compared to that at the respective optimum pH in the presence of ZnO, TiO₂ as well
as ZnO-TiO₂. Hence the combination of US and UV is highly effective to assist in overcoming at least partially, the negative impact on degradation caused by the pH effect. The simultaneous sono and photo activation of the catalyst serves to lessen the effect of pH on the surface characteristics of the catalyst. However, it is rather complex to analyze or predict the precise effect of the pH on the sono, photo or sonophotocatalytic degradation of phenol on semiconductor oxides. Effect of pH on the US, UV and US+UV induced activation of ZnO, TiO₂ and ZnO-TiO₂ is summarized in Table 5.3.

![Graph](image_url)

**Fig. 5.7:** Effect of pH on the sonophotocatalytic degradation of phenol ZnO, TiO₂ and ZnO-TiO₂.
Table 5.3: Effect pH on the US, UV and US+UV induced degradation of phenol in presence of ZnO, TiO₂ and ZnO-TiO₂.

<table>
<thead>
<tr>
<th>pH</th>
<th>Percentage Degradation of phenol on ZnO</th>
<th>TiO₂</th>
<th>ZnO- TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>US</td>
<td>UV</td>
<td>US+UV</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>22.0</td>
<td>43.0</td>
</tr>
<tr>
<td>4</td>
<td>9.6</td>
<td>33.1</td>
<td>59.6</td>
</tr>
<tr>
<td>5</td>
<td>11.8</td>
<td>44.7</td>
<td>79.5</td>
</tr>
<tr>
<td>5.5</td>
<td>13.9</td>
<td>55.0</td>
<td>85.0</td>
</tr>
<tr>
<td>6</td>
<td>12.1</td>
<td>53.7</td>
<td>71.5</td>
</tr>
<tr>
<td>7</td>
<td>8.9</td>
<td>52.2</td>
<td>62.2</td>
</tr>
<tr>
<td>8</td>
<td>7.0</td>
<td>51.2</td>
<td>64.2</td>
</tr>
<tr>
<td>9</td>
<td>5.7</td>
<td>43.4</td>
<td>57.6</td>
</tr>
<tr>
<td>10</td>
<td>5.2</td>
<td>36.7</td>
<td>55.2</td>
</tr>
<tr>
<td>11</td>
<td>5.0</td>
<td>32.6</td>
<td>54.7</td>
</tr>
</tbody>
</table>

5.3.4 Effect of reaction volume

The effect of reaction volume on sonophotocatalytic degradation of phenol on ZnO, TiO₂ and ZnO-TiO₂, is investigated by varying the reaction volume keeping the other parameters constant.

The results obtained are presented in Fig. 5.8(a). It is seen that the % degradation in presence of each catalyst (ZnO, TiO₂ and ZnO-TiO₂) decreased with increase in reaction solution volume. The synergistic effect of sonophotocatalysis is visible in all cases irrespective of the volume as shown in Table 5.4. The % degradation decreases with increase in volume upto 75 mL and stabilizes thereafter. However, the actual rate of degradation in terms of the number of phenol molecules disappearing increases with increase in volume [see Fig. 5.8(b)].
Fig. 5.8(a): Effect of reaction volume on the sonophotocatalytic degradation of phenol over ZnO, TiO2 and ZnO-TiO2.

Table 5.4: Effect of reaction volume on the US, UV and US+UV induced degradation of phenol in presence of ZnO, TiO2 and ZnO-TiO2.  
[Catalyst]: [0.1g/L (ZnO-TiO2 & ZnO) & 0.25g/L (TiO2)]; pH: 5.5-6; [Phenol]: 40 mg/L; Irradiation time: 120 min

<table>
<thead>
<tr>
<th>Reaction volume (mL)</th>
<th>Percentage Degradation of phenol on ZnO</th>
<th>TiO2</th>
<th>ZnO-TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>18.9</td>
<td>70.1</td>
<td>90.7</td>
</tr>
<tr>
<td>50</td>
<td>13.1</td>
<td>54.3</td>
<td>85.0</td>
</tr>
<tr>
<td>75</td>
<td>12.5</td>
<td>42.4</td>
<td>78.9</td>
</tr>
<tr>
<td>100</td>
<td>10.8</td>
<td>31.1</td>
<td>76.9</td>
</tr>
</tbody>
</table>

The rate of increase with volume slows down at higher volumes. The increase in rate with increase in volume can be attributed to the increase in the number of active cavitation bubbles per unit volume and
consequent increase in the number of reactive free radicals formed in the system and their interaction with the increasingly available substrate.

![Graph](image)

**Fig. 5.8(b): Effect of reaction volume on the rate of degradation of phenol.**

This reduction of the rate increase with increase in volume in the same reactor is attributed to the increase in the thickness of the irradiated region which results in attenuation of the UV/US intensity through the solution [203]. The slowdown in the rate is also caused possibly by eventual absorption of ultrasonic energy by the medium and its dissipation less productively. The enhancement in the degradation of phenol by (US+UV) over the degradation in presence of US or UV individually is higher at all volumes. This again confirms the potential of the combination of US and UV to accelerate the degradation of organic pollutants in water even under unfavorable conditions.
5.3.5 Effect of particle size

The particle size of catalyst influences the catalyst activity inversely mainly due to decreasing surface area with increase in particle size. This has been proven in the case of sono and photocatalysis in earlier chapters. The influence of catalyst loading also points to the possibility of surface availability related effect on the degradation. Hence, degradation experiments were conducted with ZnO, TiO₂ and ZnO-TiO₂ of various particle sizes and the results obtained are shown in Fig 5.9. The effect is not significant for any of the catalysts, at least in the range of 4 to 16 µm studied.

![Figure 5.9: Effect of particle size on the sonophotocatalytic degradation of phenol over ZnO, TiO₂ and ZnO-TiO₂](image)

- [Phenol] - 40 mg/L
- Catalyst loading: ZnO & ZnO-TiO₂ - 0.1 g/L, TiO₂ - 0.25 g/L
- pH - 5.5 - 6
- Vol. - 50 mL
- Time - 120 min

Fig 5.9: Effect of particle size on the sonophotocatalytic degradation of phenol over ZnO, TiO₂ and ZnO-TiO₂
The inverse relation between particle size of the catalyst and the degradation of phenol is more significant in photocatalysis as shown in chapter 3. Decrease in particle size leads to increase in surface area, more surface sites for adsorption of the pollutant, more efficient absorption of light and better surface promoted interaction between the reactants resulting in higher conversion. However, in the case of sonophotocatalysis, the synergy as a result of the combination of UV and US is adequate to compensate for the decrease in photocatalysis due to increase in particle size. Further, the US itself leads to deaggregation as well as decrease in particle size and enhanced surface area. Hence, the particle size effect is not very significant in sono or sonophotocatalysis.

5.3.6 Effect of aeration/deaeration

The important role of dissolved O$_2$ in sono and photocatalysis was discussed in previous chapters. The effect of dissolved air/oxygen on the sonophotocatalytic degradation of phenol was also tested by purging the system with N$_2$ for 1 hr in the presence of each of the three catalysts. The results are as shown in Table 5.5. The degradation is inhibited in the system purged with N$_2$. Bubbling with air enhances the degradation because of increased supply of O$_2$ including the replenishment of consumed O$_2$. This confirms that dissolved oxygen has a significant role in the sonophotocatalytic degradation of phenol also for the reasons explained and discussed in earlier chapters.
Table 5.5: Effect of N₂/air/purging of the reaction system on the sonophotocatalytic degradation of phenol.
[Catalyst]: [0.1g/L (ZnO-TiO₂ & ZnO) & 0.25g/L (TiO₂)]; [phenol]: 40 mg/L; pH: 5.5; Reaction Volume: 50 ml; Irradiation Time: 120 min

<table>
<thead>
<tr>
<th>Purging gas</th>
<th>Percentage Degradation of phenol under US+UV on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnO</td>
</tr>
<tr>
<td>None</td>
<td>85</td>
</tr>
<tr>
<td>N₂</td>
<td>41</td>
</tr>
<tr>
<td>Air</td>
<td>96</td>
</tr>
</tbody>
</table>

Comparative effect of purging the reaction solution with N₂ and air on the sono, photo and sonophotocatalytic degradation of phenol is given in Table 5.6.

Table 5.6: Comparative effect of N₂/air/purging of the reaction system on the US, UV and US+UV degradation of phenol.
[Catalyst]: [0.1g/L (ZnO-TiO₂ & ZnO) & 0.25g/L (TiO₂)]; [phenol]: 40 mg/L; pH: 5.5; 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></td>
<td>US</td>
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<tr>
<td>None</td>
<td>14</td>
</tr>
<tr>
<td>N₂</td>
<td>9</td>
</tr>
<tr>
<td>Air</td>
<td>19</td>
</tr>
</tbody>
</table>

5.4 Mechanism of the Sonophotocatalytic degradation

The mechanism of sonophotocatalysis is essentially a combination of sono and photocatalysis which have been explained in earlier chapters. The combination of the two processes provides synergy and consequently, the combined effect is more than the simple additive effect. The general mechanism of sonophotocatalysis can be summarized as follows:
Sonolysis of water produces active radicals H· and OH· via cavitation which attack organic compounds in solution. The presence of a highly heterogeneous environment such as the catalyst particles in the reaction mixture enhances this phenomenon as the microbubbles tend to break up into smaller ones. This will increase the total number of regions of high temperature and pressure. Dissolved oxygen present in the system serves as a source for nucleus cavitation. Thus the number of OH radicals produced by the system increases leading to oxidation of phenol even in the absence of light. In addition to the production of free radicals, sonolysis can also result in the pyrolysis of vaporized molecules and shear stress. Sonication of pure water has been shown to result in the following chain reactions which are accelerated by the presence of suspended solid particles [32].

\[
\begin{align*}
H_2O & \rightarrow H^+ + \cdot OH & (127) \\
H^+ + \cdot OH & \rightarrow H_2O & (128) \\
\cdot OH + \cdot OH & \rightarrow H_2O_2 & (129) \\
2\cdot OH & \rightarrow H_2O + O^+ & (130)
\end{align*}
\]

Further, the following reactions (which are shown in section 4.3.9., chapter 4) can occur in presence of oxygen.

\[
\begin{align*}
O_2 & \rightarrow 2\cdot O & (131) \\
O_2 + \cdot O & \rightarrow O_3 & (132) \\
O_2 + ^H & \rightarrow 2\cdot O (or O+ \cdot OH) & (133) \\
\cdot O + ^O_2 H & \rightarrow \cdot OH + O_2 & (134) \\
\cdot O + H_2O & \rightarrow 2\cdot OH & (135) \\
2\cdot O_2 H & \rightarrow H_2O_2 + O_2 & (136)
\end{align*}
\]
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Various active species produced as above react with phenol in the bulk solution or at the interface between the bubbles and the liquid phase. The ozone produced as above can also promote the degradation of phenol in combination with UV via the direct and indirect production of hydroxyl radicals.

$$O_3 + h\nu \rightarrow O_2 + O$$ .............................................................. (137)

$$O^+ + H_2O \rightarrow \cdot OH + \cdot OH$$ .................................................... (138)

$$O + H_2O \rightarrow H_2O_2$$ ................................................................. (139)

$$H_2O_2 + h\nu \rightarrow \cdot OH + \cdot OH$$ ................................................... (140)

$H_2O_2$ as well as the reactive radical species can interact with phenol, leading to its degradation and eventual mineralization.

Further sonolysis of the semiconductor is also known to lead to sonoluminescence which can result in photocatalytic degradation. Under concurrent UV irradiation, the direct photocatalytic reaction becomes the most dominant route making the sonoluminescence initiated photocatalysis a minor player. The overall photocatalytic process can be summarized as:

Generation of electron – hole pairs from UV radiation striking the semiconductor (SC)

$$SC + h\nu \rightarrow h^+ + e^-$$ ................................................................. (141)

Recombination of electron – hole pairs

$$h^+ + e^- \rightarrow \text{Heat}$$................................................................. (142)

Formation of primary radicals by valence band holes
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\[ h^+ + OH^- \rightarrow OH^- \] ........................................................................... (143)

\[ h^+ + H_2O \rightarrow OH^- + H^+ \] ........................................................................... (144)

Scavenging of conduction band electrons by O₂

\[ e^- + O_2 \rightarrow \cdot O_2^- \] .................................................................................. (145)

Formation of multiple peroxide species

\[ H^+ + O_2^- \rightarrow HO_2^- \] ..................................................................................... (146)

\[ HO_2^- + e^- + H^+ \rightarrow H_2O_2 \] ............................................................................ (147)

\[ \text{Phenol + Reactive Oxygen Species (} O_2^-, HO_2^-, OH^-) \rightarrow \text{Intermediates} \rightarrow H_2O + CO_2 \] ........................................................................ (148)

US is known to have the ability to disperse agglomerated particles. Deagglomeration of catalyst particles can increase the overall surface area, provide more active sites for adsorption of the reactant, enhance the absorption of US/UV and generate more reactive species. This can lead to synergy in the degradation. In order to verify this, the photocatalytic reaction was interrupted periodically (for 3 min each after 15, 45, 75 and 105 min of UV irradiation) by removing the reaction system from UV light and subjecting it to US during the interruption. The results are summarized in Table 5.7.

Table 5.7: Photocatalytic removal of phenol with and without interruption of UV irradiation [ZnO]: 0.1 g/L; pH: 5.5; volume: 50 mL; [Phenol]: 40 mg/L.

<table>
<thead>
<tr>
<th>UV irradiation time (min)</th>
<th>Percentage removal of phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uninterruption of UV</td>
</tr>
<tr>
<td>30</td>
<td>21.2</td>
</tr>
<tr>
<td>60</td>
<td>43.1</td>
</tr>
<tr>
<td>120</td>
<td>56.9</td>
</tr>
</tbody>
</table>

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In the case of experiments with periodic short interruption of UV with US, there is enhancement in the degradation of phenol. Since the US was used only for a short period, the influence of sonolysis other than deagglomeration is expected to be minimal. Hence, the enhancement can be attributed to deagglomeration and associated advantages. The extent of enhancement remains more or less the same (6–8%) in all cases, indicating that US has only limited influence when applied independently. Further, the enhancement is much less compared to that from simultaneous (UV + US) irradiation (~ 85% after 120 min) thereby confirming the synergistic role of US in presence of UV. Hence deagglomeration is not the only factor that contributes to the US induced synergy even though its contribution could be important. Another major factor for the synergy may be the ability of US to prevent the deactivation of the catalyst by removing adsorbed moieties from the surface by microstreaming and microbubbles’ eruption [19]. This kind of surface cleaning can contribute to enhanced reaction only by the simultaneous use of US and UV because microstreaming and microbubbling can only occur in the solution during the instantaneous moment when US is applied. The current observation that the increase in degradation, when the UV is interrupted by US is only marginal irrespective of the duration of US irradiation, suggests that the synergy is operational only when US and UV are applied simultaneously.

According to Naffrechoux et al. [209] the synergy in sonophotocatalytic systems can be attributed to the US induced physical changes in the catalyst and consequent benefits coupled with concurrent action of three oxidation mechanisms – (i) photodegradation,
(ii) sonodegradation and (iii) ozone oxidation. This is consistent with the observation made here and the mechanism proposed.

5.5 Effect of anions

The importance of investigating the effect of anions on the degradation of water pollutants by AOPs has been discussed earlier. In this context, the effect of some of the anions commonly found in water on the sonophotocatalytic degradation of phenol in presence of ZnO, TiO\textsubscript{2} and ZnO-TiO\textsubscript{2} is investigated. The results are presented in Fig.5.10 (a, b and c).

![Fig.5.10(a): Effect of anions on the sonophotocatalytic degradation of phenol over ZnO](image-url)
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Fig. 5.10(b): Effect of anions on the sonophotocatalytic degradation of phenol over TiO₂

Fig. 5.10(c): Effect of anion on the sonophotocatalytic degradation of phenol over ZnO-TiO₂

Unlike in the case of sono and photocatalysis in which some anions enhance the degradation of phenol, in the case of sonophotocatalysis almost all anions investigated inhibit the degradation. The inhibition by I⁻, Br⁻ and
CO$_3^{2-}$ is relatively less and may be treated as almost insignificant in the case of ZnO and TiO$_2$. In the case of ZnO-TiO$_2$ also, the inhibition by these ions is not much. It may be generally stated that in the case of all three catalysts the anion I$^-$, Br$^-$ and CO$_3^{2-}$ do not have any significant effect on the sonophotocatalytic degradation of phenol. In the case of F$, the effect is not consistent, with inhibition in presence of ZnO and ZnO-TiO$_2$ and no significant effect in the case of TiO$_2$. The inconsistent behaviour of F$^-$ is seen in photocatalysis also. Anions PO$_4^{3-}$, SO$_4^{2-}$, Cl$^-$ and NO$_3^-$ inhibit the degradation in all cases. The inhibition can be partially attributed to the scavenging of reactive OH radicals by the anions. The radical anion formed by interaction of OH and the anion are not as effective as the OH to effect the degradation of the pollutant, thus leading to the inhibition. Being relatively large in size, they can also form layers on the catalyst surface thereby inhibiting the activation of the catalyst surface. In any case, the highly efficient sonophotocatalysis is capable of overcoming the inhibitor effect by most anions as seen in the case of all three catalysts.

The inhibition follows the order:

ZnO: SO$_4^{2-}$ > F$^-$ > PO$_4^{3-}$ > NO$_3^-$ > Cl$^-$ > Br$^-$ > CO$_3^{2-}$ ≈ I$^-$

TiO$_2$: NO$_3^-$ ≈ PO$_4^{3-}$ > SO$_4^{2-}$ > Cl$^-$ > CO$_3^{2-}$ > Br$^-$ ≈ I$^-$ ≥ F$^-$

ZnO- TiO$_2$: NO$_3^-$ > SO$_4^{2-}$ > PO$_4^{3-}$ > Cl$^-$ > Br$^-$ ≥ F$^-$ ≥ I$^-$ ≥ CO$_3^{2-}$

However, the influence of anion on AOPs, as brought out in earlier chapters also, is very complex and inconsistent and hence cannot be generalized. Factors such as concentration of the anion, concentration of substrate, catalyst loading, type of intermediates formed, interaction in the bulk as well as on the surface can influence the effect of anions.
The comparative effect of these anions on the sono, photo and sonophotocatalytic degradation of phenol is summarized in Fig. 5.11 (a - x)

**Fig. 5.11 (a):** Effect of F⁻ on US, UV and US+UV initiated degradation of phenol in presence of ZnO.

**Fig. 5.11 (b):** Effect of F⁻ on US, UV and US+UV initiated degradation of phenol in presence of TiO₂.
Fig. 5.11 (c): Effect of F\textsuperscript{-} on US, UV and US+UV initiated degradation of phenol in presence of ZnO-TiO\textsubscript{2}.

Fig. 5.11 (d): Effect of Cl\textsuperscript{-} on US, UV and US+UV initiated degradation of phenol in presence of ZnO.
Fig. 5.11 (e): Effect of Cl⁻ on US, UV and US+UV initiated degradation of phenol in presence of TiO₂.

Fig. 5.11 (f): Effect of Cl⁻ on US, UV and US+UV initiated degradation of phenol in presence of ZnO-TiO₂.
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Fig. 5.11 (g): Effect of Br⁻ on US, UV and US+UV initiated degradation of phenol in presence of ZnO.

Fig. 5.11 (h): Effect of Br⁻ on US, UV and US+UV initiated degradation of phenol in presence of TiO₂.
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**Fig. 5.11 (i):** Effect of Br⁻ on US, UV and US+UV initiated degradation of phenol in presence of ZnO-TiO₂.

**Fig. 5.11 (j):** Effect of I⁻ on US, UV and US+UV initiated degradation of phenol in presence of ZnO.
Fig. 5.11 (k): Effect of I⁻ on US, UV and US+UV initiated degradation of phenol in presence of TiO₂.

Fig. 5.11 (l): Effect of I⁻ on US, UV and US+UV initiated degradation of phenol in presence of ZnO-TiO₂.
Fig. 5.11 (m): Effect of $\text{CO}_3^{2-}$ on US, UV and US+UV initiated degradation of phenol in presence of ZnO.

Fig. 5.11 (n): Effect of $\text{CO}_3^{2-}$ on US, UV and US+UV initiated degradation of phenol in presence of TiO$_2$. 
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Fig. 5.11 (o): Effect of CO$_3^{2-}$ on US, UV and US+UV initiated degradation of phenol in presence of ZnO-TiO$_2$.

Fig. 5.11 (p): Effect of NO$_3^-$ on US, UV and US+UV initiated degradation of phenol in presence of ZnO.
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**Fig. 5.11 (q):** Effect of NO$_3^-$ on US, UV and US+UV initiated degradation of phenol in presence of TiO$_2$.

**Fig. 5.11 (r):** Effect of NO$_3^-$ on US, UV and US+UV initiated degradation of phenol in presence of TiO$_2$. 
Fig. 5.11 (s): Effect of SO$_4^{2-}$ on US, UV and US+UV initiated degradation of phenol in presence of ZnO.

Fig. 5.11 (t): Effect of SO$_4^{2-}$ on US, UV and US+UV initiated degradation of phenol in presence of TiO$_2$. 

[Diagram showing the percentage degradation of phenol under different conditions: US, UV, and US+UV with and without SO$_4^{2-}$ in presence of ZnO and TiO$_2$.]

[Legend for graphs: ZnO+Phenol, ZnO+Phenol+SO$_4^{2-}$, TiO$_2$+Phenol, TiO$_2$+Phenol+SO$_4^{2-}$]