Periodic Change in the Concentration of Hydrogen peroxide Formed during the Semiconductor Mediated Sonocatalytic treatment of Wastewater: Investigations on pH Effect and Other Operational Variables

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Abstract

Hydrogen peroxide, formed in situ or externally added, is an important Reactive Oxygen Species (ROS) involved in Advanced Oxidation Processes (AOP) such as sono, photo and sonophoto catalysis being investigated as environment friendly technologies for the treatment of wastewater under ambient conditions. Among the various ROS such as ‘OH, HO₂, O₂⁺, H₂O₂, O₂ etc, H₂O₂ is the most stable and it serves as a reservoir of other ROS. Current investigations on the ZnO and TiO₂ mediated sonocatalytic degradation of phenol pollutant in water reveal that, H₂O₂ formed cannot be quantitatively correlated with the degradation of the pollutant. The concentration of H₂O₂ varies in a wavelike fashion (oscillation) with well defined crests and troughs, indicating concurrent formation and decomposition. Both processes are sensitive to the reaction conditions and depending on the externally forced or in situ situation, either of them can predominate. The degradation of H₂O₂ continues for some more time even after the sonication has been put off showing that the catalyst has some residual activity. This further confirms that trapped electrons and holes have unusually longer life even after the irradiation is off. Concentration of H₂O₂, catalyst loading, dissolved gases, concentration of the organic pollutant, pH etc influence the oscillation. The degradation of phenol is favored in the acidic range with maximum at pH 5.5. The successive maxima and the minima in the oscillation of H₂O₂ concentration also are higher in the acidic range. The influence of pH on various factors leading to the oscillation in the concentration of H₂O₂ is unequivocally established from a number of experiments, for the first time in this paper. An appropriate mechanism to explain the complex phenomenon is also proposed.

Keywords: Sonocatalysis, zinc oxide, titanium dioxide, hydrogen peroxide, oscillation, pH effect.

Introduction

Considerable interest has been shown in the application of sonocatalysis, photocatalysis and its combination sonophotocatalysis using suspended semiconductor oxide particles for the environment–friendly destruction of organic pollutants in water. Major advantages of these Advanced Oxidation Processes (AOP) include relatively mild reaction conditions and their proven ability to degrade several toxic refractory pollutants. Of these, photocatalysis has been investigated extensively with semiconductors such as TiO₂ and ZnO as catalysts for the removal of a variety of pollutants. However, many of these catalysts are active only in the UV range, which make them unattractive for solar energy harvesting. Several efforts are being made to make visible light active photocatalysts. These include dye sensitization, semiconductor coupling, impurity doping, use of coordination metal complexes and metal deposition. Composites such as TiO₂/carbon have also been reported. Deposition of noble metals such as Pt, Pd, Au, Ag etc on TiO₂ enhances the catalytic oxidation of organic pollutants.

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. 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. Coupling US with Ultraviolet (UV) irradiation enhances the efficiency of semiconductor mediated degradation of aqueous pollutants synergistically.

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. The temperature of the gaseous contents of a collapsing cavity can reach approximately 5500°C and that of the liquid immediately surrounding the cavity reaches up to 2100°C. The localized pressure is estimated to be around 500 atmospheres resulting in the formation of transient supercritical water. 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\(^{2-}\) 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.

Studies in our laboratory have shown that H\(_2\)O\(_2\), one of the major products of sonocatalytic degradation of organic pollutants in water, undergoes simultaneous formation and decomposition during the degradation process\(^5\),\(^2\). This results in oscillation in the concentration of H\(_2\)O\(_2\). The rate of degradation of the pollutants and the oscillation phenomenon are influenced by various reaction parameters such as catalyst loading, substrate concentration, reaction volume, presence of anions, reaction intermediates, pH etc. The effect of pH on sonocatalytic degradation of pollutants in water is more complex. In this study the effect of pH on sonocatalytically formed H\(_2\)O\(_2\) in presence of ZnO is investigated in detail.

### Materials and Methods

ZnO and TiO\(_2\) used in the study were supplied by Merck India Limited. In both cases the purity was over 99%. The surface areas of TiO\(_2\) and ZnO, as determined by the BET method are approximately 15 and 12 m\(^2\)/g respectively. The average particle size of both ZnO and TiO\(_2\) was 10 µm. Phenol AnalR Grade (99% purity) from Qualigen (India) was used as such without further purification. All other chemicals were of AnalR Grade or equivalent. The sonocatalytic reactions were performed as reported earlier\(^6\). The concentration of phenol left behind was analyzed periodically by Spectrophotometry at 500 nm. H\(_2\)O\(_2\) is determined by iodometry\(^2\)\(^3\). Mineralization was identified by the evolution of CO\(_2\).

### Results and Discussion

Investigations on the sonocatalytic degradation of phenol using ZnO catalysts showed that no significant degradation took place in the absence of ultrasound or the catalyst suggesting that both catalyst and sound are essential to effect reasonable degradation. However, small quantity of phenol degraded under US irradiation even in the absence of catalysts (see figure 1).

![Sonocatalytic degradation of phenol](image-url)
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 solution25.

\[
H_2O \rightarrow H^+ + OH^- \quad (1)
\]

The free radicals thus produced can lead to the formation of H2O2 and degradation of phenol as follows:

\[
\begin{align*}
H^+ + O_2 & \rightarrow HO^\cdot \quad (2) \\
HO^\cdot + HO^\cdot & \rightarrow H_2O_2 \quad (3) \\
2OH^- & \rightarrow H_2O_2 \quad (4)
\end{align*}
\]

Reactive oxygen species (OH, HO2•, etc) + phenol → Intermediates → H2O + CO2 (5)

However, there was no continuous increase in the concentration of H2O2 after the initial period possibly due to its parallel decomposition into water and oxygen as well as participation in the degradation of phenol5,16,23. At the same time the removal of phenol continued, though at a very slow rate.

The sonocatalytic degradation of phenol in presence of ZnO and TiO2 at respective optimized loadings is shown in figure 2a. The fate of H2O2 formed in presence of these catalysts is shown in figure 2b.

Sonochemical processes in aqueous media are facilitated in a heterogeneous environment such as the presence of suspended particles24,25. The presence of the particles help to break up the microbubbles created by US into smaller ones, thus increasing the number of regions of high temperature and pressure. This leads to increase in the number of reactive OH radicals which will interact with the organic pollutants present in water and oxidise them, resulting in eventual mineralization. The increase in the optimum concentration of H2O2 in presence of particles was reported by Keck etal26. Instances of decrease in the concentration of H2O2 in presence of particles have also been reported19. Our studies presented in this report as well as in earlier papers show that both increase and decrease in the concentration of H2O2 is possible in the same system depending on the relative concentration of H2O2 and the substrate as well as other reaction parameters5,23.

The effect of ZnO loading on the sonocatalytic formation of H2O2 is shown in figure 3a. Catalyst loading for highest maximum in the oscillation curve of H2O2 is 50 mg/L. Optimum loading for the degradation of phenol is 100 mg/L (fig 3b).

**Fig 2(a): Sonocatalytic degradation of phenol in presence of ZnO and TiO2**
Fig 2(b): Fate of \( \text{H}_2\text{O}_2 \) during the sonocatalytic degradation of phenol in presence of ZnO and TiO\(_2\).

Fig 3(a): Effect of catalyst loading on the oscillation in the concentration of \( \text{H}_2\text{O}_2 \).
Fig 3(b): Effect of catalyst loading on the degradation of phenol

Fig 4: Effect of particle size on the initial rate of H$_2$O$_2$ formation
Since the formation and decomposition of H$_2$O$_2$ is occurring in parallel all the time, optimization of catalyst loading with respect to H$_2$O$_2$ formation may not be reliable. Hence the optimum loading of ZnO for phenol degradation is taken as the basis for further studies on the oscillation in the concentration of H$_2$O$_2$.

At the optimized loading for phenol degradation, the effect of particle size on the H$_2$O$_2$ formation is examined. The sonocatalytic rate of degradation of phenol increases with decrease in the particle size up to an optimum value. The effect of particle size of ZnO on the H$_2$O$_2$ formed in the system is shown in figure 4.

With increase in particle size in the range of 6-60 micron, the initial rate of H$_2$O$_2$ formation decreases slightly from $1.4 \times 10^3$ to $1.1 \times 10^3$ mg/L/sec possibly due to lower surface area and decrease in the rate of generation of OH radicals. However, the nature of the oscillation curve remains the same in all cases even though the maxima of H$_2$O$_2$ concentration in the oscillation curve are higher at lower particle sizes. The successive maxima and minima of the oscillation curve remain more or less identical irrespective of the particle size of the catalyst. This confirms our earlier observation that the single most important factor that determines the rate of formation or decomposition of H$_2$O$_2$ is its concentration and either of them will predominate once a critical lower or upper concentration is reached respectively.

Simple quartz or alumina particles have very little effect on the sonochemical removal of phenol thereby indicating that it is not just the particle effect that promotes sonocatalytic degradation of phenol in the case of semiconductor oxides such as ZnO, which can act catalytically. However the concentration of sonochemically formed H$_2$O$_2$ increases initially in the presence of quartz, Al$_2$O$_3$ and ZnO in the order ZnO > quartz > alumina > no particles.

The higher yield of H$_2$O$_2$ by sonolysis in presence of particles is explained by Keck et al. on the assumption that the bubble size and collapse time are not influenced by the nature and concentrations of the particles used. But the shape of the bubbles may have changed from spherical to asymmetric. The larger surface of these bubbles enable more radicals to escape into the bulk forming more H$_2$O$_2$ or react with more organic molecules in the bulk.

**Effect of Phenol on H$_2$O$_2$:** Formation of H$_2$O$_2$ is reported in the case of sonocatalytic and photocatalytic degradation of phenol in presence of ZnO, TiO$_2$ and ZnO-TiO$_2$ catalysts. In the case of US irradiation, H$_2$O$_2$ is produced even in the absence of phenol indicating the formation of free radicals OH and HO$_2$ in liquid water by US. The concentration of H$_2$O$_2$ 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$_2$O$_2$. This is confirmed by experiments with added H$_2$O$_2$ which show that H$_2$O$_2$ enhances the degradation of phenol significantly in the beginning.

However this high rate of enhancement is not sustained later on, probably because thermal decomposition of H$_2$O$_2$ to water and oxygen rather than to reactive radical species may be occurring in presence of US. The decomposition and consequent decrease in the concentration of H$_2$O$_2$ is more evident in the initial stages in the case of TiO$_2$. The maximum concentration of H$_2$O$_2$ reached is different for different catalysts under otherwise identical conditions, indicating that it is dependent on the nature of the catalyst. It also implies that the role of the semiconductor oxide is not limited to just particle effect. In the beginning, added H$_2$O$_2$ decomposes faster producing maximum OH radicals which can degrade phenol. However, the decomposition of H$_2$O$_2$ 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$_2$O$_2$, the H$_2$O$_2$ formed insitu will be accelerating the reaction rate. Hence the effect of initially added H$_2$O$_2$ is not that prominent in the later stages of the reaction.

The effect of concentration of phenol on the rate of degradation has been investigated earlier. The degradation increases with increase in the concentration of phenol up to 40 mg/L beyond which it levels off or decreases slightly, due to saturation of the catalyst surface. In the case of oscillation of H$_2$O$_2$, also the effect of concentration is fairly similar. At the optimum concentration for phenol degradation (30-40 mg/L) (figure 5), the maxima in H$_2$O$_2$ concentration in the oscillation curve also are the highest indicating a direct correlation between the rate of phenol degradation and the oscillation.

**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. Previous studies have shown that the degradation is more efficient in the acidic region than in the alkaline region and 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. The effect of pH on the fate of H$_2$O$_2$, especially the oscillation in its concentration resulting from simultaneous formation and decomposition has not been investigated so far. Fig 6 shows the concentration of H$_2$O$_2$ in the system at different times during the sonocatalytic degradation of phenol on ZnO at different pH.
Table 1
Effect of added $\text{H}_2\text{O}_2$ on the sonocatalytic degradation of phenol in presence of ZnO and TiO$_2$

<table>
<thead>
<tr>
<th>Reaction Condition</th>
<th>% Degradation of phenol without added $\text{H}_2\text{O}_2$</th>
<th>% Degradation of phenol with added $\text{H}_2\text{O}_2$</th>
<th>% enhancement by added $\text{H}_2\text{O}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 min</td>
<td>60 min</td>
<td>90 min</td>
</tr>
<tr>
<td>US (ZnO)</td>
<td>1.1</td>
<td>6.0</td>
<td>9.5</td>
</tr>
<tr>
<td>US (TiO$_2$)</td>
<td>0.8</td>
<td>3.7</td>
<td>5.2</td>
</tr>
</tbody>
</table>

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

Fig 5: Effect of concentration of phenol on the oscillation in the concentration of $\text{H}_2\text{O}_2$ formed during the sonocatalytic degradation of phenol

Fig 6: Effect of pH on the oscillation in the concentration of $\text{H}_2\text{O}_2$ during the sonocatalytic degradation of phenol
The oscillation as well as the maxima in the concentration of H$_2$O$_2$ is more pronounced in the acidic region. This is consistent with the observations on the sonocatalytic degradation of phenol on ZnO in which maximum degradation is observed at in the range of pH 5.5 to 6. The relatively lower maxima and minima at pH 3 are probably because of the corrosion of ZnO which reduces the effective surface sites for the formation of OH radicals and subsequent interactions. In order to decipher the effect of phenol on the oscillation, the sonocatalytic decomposition of H$_2$O$_2$ on ZnO was investigated (in the absence of phenol) under identical conditions (Figure 7).

In this case also the concurrent formation and decomposition of H$_2$O$_2$ is seen at all pH. Comparison of the results in the presence as well as the absence of phenol shows that the oscillation is more significant in presence of phenol. This illustrates the importance of interaction between the free radicals generated and phenol. This is further verified by adding phenol in between to the sonocatalytic system containing only H$_2$O$_2$ (see Figure 8).

At pH 5.5 where the adsorption and degradation of phenol is maximum, the H$_2$O$_2$ formation is accelerated by phenol addition. At pH 3 and 11 where the degradation of phenol is relatively less, addition of phenol in between does not influence the oscillation as much as at pH 5.5. This reiterates the influence of phenol on the phenomenon of oscillation. Addition of H$_2$O$_2$ into the phenol-ZnO sonocatalytic system in between the reaction does not alter the course of oscillation significantly at pH 3, 5.5 or 11. This indicates that there is a critical range of H$_2$O$_2$ concentration in which the oscillation is quite facile. Beyond this, any addition of H$_2$O$_2$ will make the system over-saturated and it is difficult to distinguish the relatively smaller increase or decrease in the concentration of in situ formed H$_2$O$_2$. Addition of extra amounts of ZnO in between to an oscillating system containing phenol enhances the maxima in the oscillation curve. This suggests that the formation of OH radicals is accelerated, which in turn can result in enhanced degradation of phenol and production of more H$_2$O$_2$. Thereafter the oscillation continues with a higher maxima and minima (figure 9).

![Graph showing effect of pH on the fate of added H$_2$O$_2$ during sonication in presence of ZnO](image_url)
Fig 8: Effect of in between addition of phenol (after 60 min) at various pH on the oscillation in the concentration of H$_2$O$_2$

Fig 9: Effect of in between addition of ZnO (after 60 min) on the oscillation in the concentration of H$_2$O$_2$
Fig 10: Memory effect of ZnO on the oscillation in the concentration of $\text{H}_2\text{O}_2$

Figure 10

Fig 11: Effect of deaeration on the oscillation in the concentration of $\text{H}_2\text{O}_2$
It has been reported that trapped electrons and holes on the surface of TiO2 have an unusually long life time extending to hours after the irradiation source is put off. Such long lived electrons and holes can react with H2O2 resulting in minor change in its concentration even after the US is off. However, the results are not exactly reproducible and the memory effect does not seem to be significant enough to merit any detailed investigation at this stage. Deaeration by bubbling the system with nitrogen does not affect the oscillation significantly (see figure 11).

Sono and photocatalytic reactions are known to require the presence of efficient electron acceptors so that the recombination of the electrons and holes at the surface can be prevented. Fast recombination between electrons and holes inhibits the interfacial charge transfer and the reactions that follow. Dioxygen molecules are efficient electron acceptors and hence sono or photocatalytic reactions do not occur in the absence of oxygen. The observation that the oscillation in the concentration of H2O2 is not affected by deaeration shows that in the absence of O2, H2O2 will serve as an electron acceptor as follows: H2O2(ad) + e− → OH(ad) + HO−(ad). (6)

The minimum in the oscillation curve is lower in the case of deaerated system which indicates that the H2O2 decomposition is proceeding even in the absence of oxygen. Hence the recombination of electrons and holes is not taking place. That means H2O2 behaves uniquely by playing the role of electron and hole scavenger in the same system as in reactions 6 and 7. H2O2(ad) + O2/h+ → HO2(ad) + H2O/H+. (7)

Such behavior by H2O2 has been proven in the case of photocatalysis by using Cavity Ring Down Spectroscopy (CRDS). The electron or hole transfer to H2O2 generates HO2− or OH− as above which may further react on the surface or get desorbed into the bulk. Such desorption of OH− radicals from the TiO2 surface has been confirmed by single molecule imaging using Fluorescence Microscopy as well as Laser Induced Fluorescence Spectroscopy. The desorption of HO2− (formed by the decomposition of H2O2) from the surface was confirmed by CRDS. Once the concentration of H2O2 has fallen below a critical point, O2 can compete effectively as an electron acceptor and the cycle of oscillation continues.

The behavior of phenol is different at different pH. This can influence the fate of H2O2 also at respective pH. In weakly acidic solution, most of the phenol molecules remain undissociated. Hence maximum number of phenol molecules can be adsorbed onto the surface resulting in increased degradation and correspondingly more H2O2. Hence the amount of H2O2 at the maximum of the curve is more. In the alkaline medium, the surface of TiO2 is negatively charged and the phenolate intermediate may be repelled away from the surface. Further, sonication effects also favor higher degradation in the acidic pH. When the pH exceeds 10, the pKw of phenol at 25°C, ionic species of phenol will be predominant. When the pH is less than the pKw, molecular species will dominate. Under sonication, the phenolate ions are concentrated in the gas-water interface of the bubbles where the hydrophobicity is strong and cannot vaporize into the cavitation bubbles. They can react only outside of the bubble film with the OH radicals cleaved from water. However, in the molecular state, phenol enters the gas-water interface of bubbles and even vaporizes into cavitation bubbles. They can react both inside by thermal cleavage and outside with OH radicals. This results in higher degradation of phenol as well as enhanced formation and decomposition of H2O2. Hence the concentration of H2O2 is more at the maxima and minima 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. 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 complex behavior of H2O2 is further aggravated by the different mechanisms of sonodegradation of phenol at different pH. Sonochemical degradation of phenol proceeds through catechol (CC), hydroquinone (HQ) and p-benzoquinone (BQ) intermediates at pH 3, CC and HQ at pH 5.7 and no detectable intermediate at pH 12. Further the sonication of HQ produces BQ while the sonication of BQ produces HQ and in both cases hydroxyl-p-benzoquinone is formed in traces as another intermediate. In this complex system consisting of too many intermediates, the exact influence of pH on the oscillatory behavior cannot be deciphered precisely.

Our results show that H2O2 decomposition is negligible in the dark or by photolysis or sonolysis in the absence of a catalyst. This is in contrast with the findings of Augugliaro et al. as well as Jenny and Pichat. Jenny and Pichat reported that the heterogeneous H2O2 decomposition is only twice faster than homogeneous decomposition while Augugliaro et al. did not find any significant difference in the decomposition with or without suspended catalyst. However Ilisz et al. observed that efficient degradation of H2O2 takes place only in presence of catalysts in photochemical systems. Their observation that the initial rate of decomposition of H2O2 decreases with decreasing concentration is reconfirmed by the current findings that in the oscillation curve of H2O2, the decomposition of H2O2 begins only when a critical maximum concentration is reached and the formation process takes over when a critical lower concentration is reached.

The overall mechanism depicting the formation of ROS and degradation of phenol is schematically presented in scheme 1. Possible steps involved in the concurrent formation and decomposition of H2O2 are given in reactions 8 to 19.
Scheme-1  Sono catalytic activation of semiconductor oxides and the formation of ROS

The formation of H$_2$O$_2$ from various ROS takes place as follows:

\[
\begin{align*}
\text{OH} + \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \\
\text{O}_2 + 2\text{e}^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \\
2\text{H}_2\text{O} + 2\cdot \text{h}^+ & \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^- \\
\text{HO}_2^- + \text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 \\
\text{O}_2^- + \text{HO}_2^- & \rightarrow \text{O}_2 + \text{HO}_2^- \\
\text{HO}_2^- + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \\
\text{P} & \rightarrow \text{P} + \text{OH} + \text{H}^+ + \cdot \text{OH} + \text{O}_2 \\
\text{H}_2\text{O}_2 + \text{h}^+ & \rightarrow \text{H}_2\text{O} + \cdot \text{OH} + \text{O}_2 \\
\end{align*}
\]

The concurrent decomposition of H$_2$O$_2$ takes place as follows:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{hv} (\lambda<380 \text{ nm}) & \rightarrow 2 \cdot \text{OH} \\
2 \cdot \text{h}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2 \text{H}^+ \\
2 \cdot \text{e}^- + 2 \text{H}^+ + \text{H}_2\text{O}_2 & \rightarrow 2 \text{H}_2\text{O} \\
\text{H}_2\text{O}_2 + \cdot \text{OH} & \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \\
\text{H}_2\text{O}_2 + \text{HO}_2^- & \rightarrow \text{H}_2\text{O} + \cdot \text{OH} + \text{O}_2 \\
\end{align*}
\]

Being a complex free radical system, other interactions leading to the formation and decomposition of H$_2$O$_2$ are also possible.

Conclusion

Hydrogen peroxide formed during the sonocatalytic degradation of phenol in water in presence of semiconductor oxides such as ZnO and TiO$_2$ undergoes concurrent formation and decomposition resulting in oscillation in its concentration. Various reaction parameters such as catalyst loading, substrate concentration, particle size, pH, externally added H$_2$O$_2$ and presence of air/O$_2$ influence the phenomenon in general and the maxima and minima in the oscillation curve in particular. H$_2$O$_2$ plays a unique role in the process as acceptor of both electrons and holes. The oscillation phenomenon continues for some more time even after the sono source is switched off, indicating the presence of memory effect in the semiconductor. A reaction mechanism based on the observations is proposed and discussed.

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References


