Oscillation in the Concentration of H_2O_2 during Advanced Oxidation Processes:TiO_2Mediated Sonocatalytic Degradation of Phenol

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Abstract:*Sono, photo and sonophotocatalysis are major Advanced Oxidation Processes (AOP) under intensive investigation as potential technologies for the removal of trace pollutants from water.The techniques involve the formation and participation of Reactive Oxygen Species (ROS) like ·OH, HO$_2$·, O$_2^-$·, H$_2$O$_2$ etc. Among these, H$_2$O$_2$ is the most stable and is also a precursor for the reactive free radicals. Current investigations on the TiO$_2$ mediated sonocatalytic degradation of phenol pollutant in water confirm our earlier findings using ZnO catalyst that H$_2$O$_2$ formed insitu cannot be quantitatively correlated with the degradation of the pollutant. The concentration of H$_2$O$_2$ formed does notincrease corresponding to phenol degradation and reaches a plateau or varies in a wave-like fashion (oscillation) with well defined crests and troughs, indicating concurrent formation and decomposition. The number of maxima and minima or their precise occurrence at any point in time is unpredictable and inconsistent, indicating the complexity of the free radical process. The influence of various reaction parameters on the oscillation are identified and investigated in detail.*

Keywords: *Hydrogen peroxide, oscillation, sonocatalysis, titanium dioxide.*

I.   INTRODUCTION

Advanced oxidation processes (AOPs) are generally used todegrade hazardous and non-biodegradable organic materials andconvert them into carbon dioxide by producing •OHradicals duringthe oxidation process. Several kinds of AOPs (e.g. ultrasound, fenton, ozone and ultraviolet light) have been effectively used in the treatment of wastewater containingpesticides, phenols and azo dyes[1-5]. Major advantages of these AOPs include relatively mild reaction conditions and proven ability to degrade several toxic refractory 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 [2-5]. Coupling US with Ultraviolet (UV) irradiation enhances the efficiency of semiconductor mediated degradation of aqueous pollutants synergistically [2, 6-8].

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 [9]. The temperature of the gaseous contents of a collapsing cavity can reach approximately 5500^0C and that of the liquid immediately surrounding the cavity reaches up to 2100^0C. The localized pressure is estimated to be around 500 atmospheres resulting in the formation of transient supercritical water [10]. The cavities are thus capable of functioning like high energy micro reactors. The consequence of these extreme conditions is the cleavage of dissolved oxygen and water molecules into radicals such as H·, OH·and O·which will react with each other as well as with H_2O and O_2 during the rapid cooling phase giving HO$_2$·and H_2O_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. Studies in our laboratory have shown that H_2O_2, one of the major products of sonocatalytic degradation of organic pollutants in water, undergoes simultaneous formation and decomposition during the degradation process [11-14]. This

results in oscillation in the concentration of H_2O_2. In this study the influence of various operational parameters on the oscillation of H_2O_2 in presence of TiO_2 under sonocatalysis is investigated in detail.

II.   MATERIALS AND METHODS

Degussa P-25 TiO_2 (99% pure) consisting of approx. 70% anatase and 30% rutile is used as such without further purification. The average particle size was around 15-20 μm and the BET surface area was ~15 m^2/g. Phenol AnalaR Grade (99% purity) from Qualigen (India) was used as such without further purification. All other chemicals were of AnalaR Grade or equivalent. The sonocatalytic reactions were performed as reported earlier [11]. The concentration of phenol left behind was analyzed periodically by Spectrophotometry at 500 nm. H_2O_2 is determined by iodometry [12]. Mineralization was identified by the evolution of CO_2.

III.   RESULTS AND DISCUSSION

Investigations on the sonocatalytic degradation of phenol using TiO_2 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 (Fig.1).
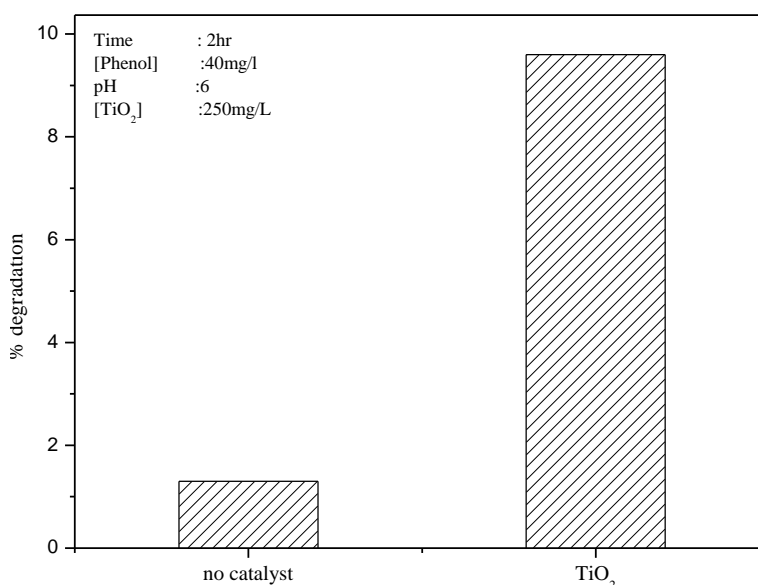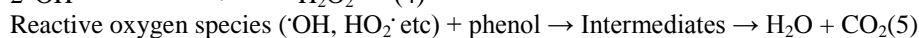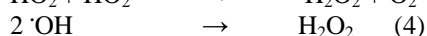

Time   : 2hr
[Phenol]   :40mg/l
pH   :6
[TiO₂]   :250mg/L

Figure 1: Sonocatalytic degradation of phenol

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 [13].

H_2O >>> $H^{\cdot} + {}^{\cdot}OH$ (1)   >>> indicates US

The free radicals thus produced can lead to the formation of H_2O_2 and degradation of phenol as follows:

$H^{\cdot} + O_2$ → $HO_2^{\cdot}$ (2)
$HO_2^{\cdot} + HO_2^{\cdot}$ → $H_2O_2 + O_2$ (3)
$2\ {}^{\cdot}OH$ → H_2O_2 (4)
Reactive oxygen species (${}^{\cdot}OH$, $HO_2^{\cdot}$ etc) + phenol → Intermediates → $H_2O + CO_2$(5)

However, there was no continuous increase in the concentration of H_2O_2 after the initial period possibly due to its parallel decomposition into water and oxygen as well as participation in the degradation of phenol [11, 12, 15]. At the same time the removal of phenol continued, though at a very slow rate.The sonocatalytic degradation of phenol as well as the fate of H_2O_2 formed in presence of TiO_2 at the optimized loadings is shown in Fig. 2aandb.
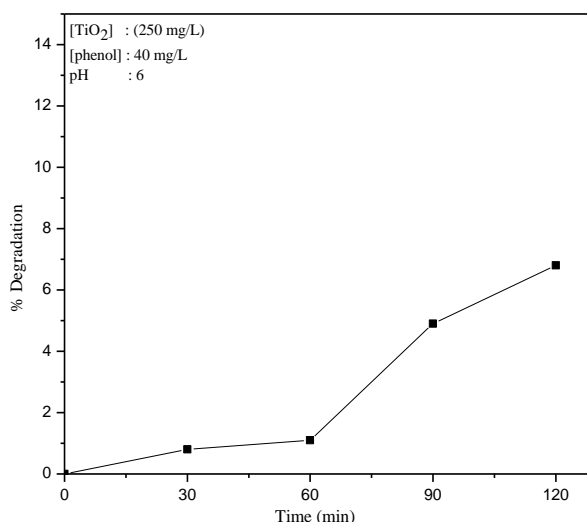
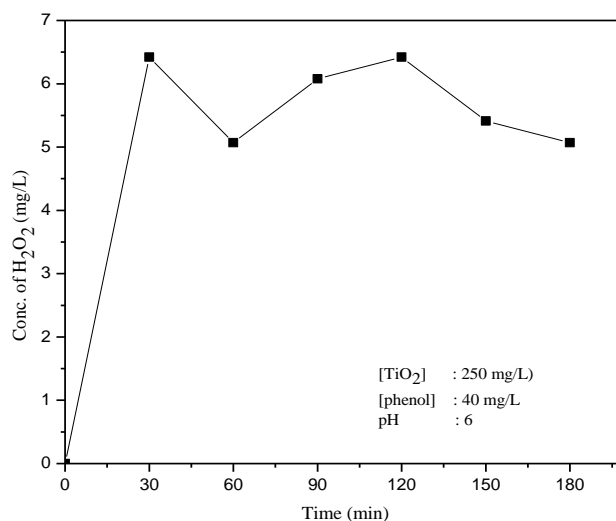**Figure 2a:** Sonocatalytic degradation of phenol in presence TiO_2

Figure 2b: Fate of H_2O_2 during the sonocatalytic degradation of phenol in presence of TiO_2

Sonochemical processes in aqueous media are facilitated in a heterogeneous environment such as the presence of suspended particles [9,10]. 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. 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 H_2O_2 in presence of particles was reported by Keck etal [16]. Instances of decrease in the concentration of H_2O_2 in presence of particles have also been reported [7]. Our studies presented in this report as well as in earlier papers show that both increase and decrease in the concentration of H_2O_2 is possible in the same system depending on the relative concentration of H_2O_2 and the substrate as well as other reaction parameters [12-14].

3.1 Effect of catalyst dosage

The effect of TiO_2 loading on the sonocatalytic degradation of phenol is shown in Fig. 3a. Optimum loading for the degradation of phenol is 0.25g/L. However, no such optimum is distinct in the case of the coproduct H_2O_2 as can be seen in Fig. 3b.
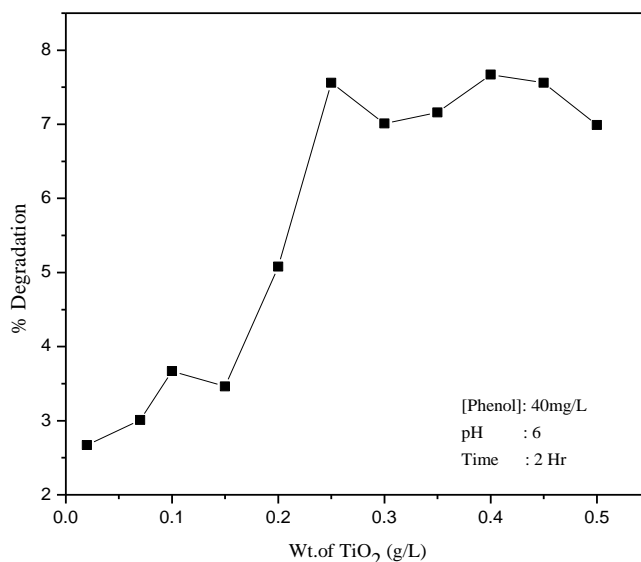
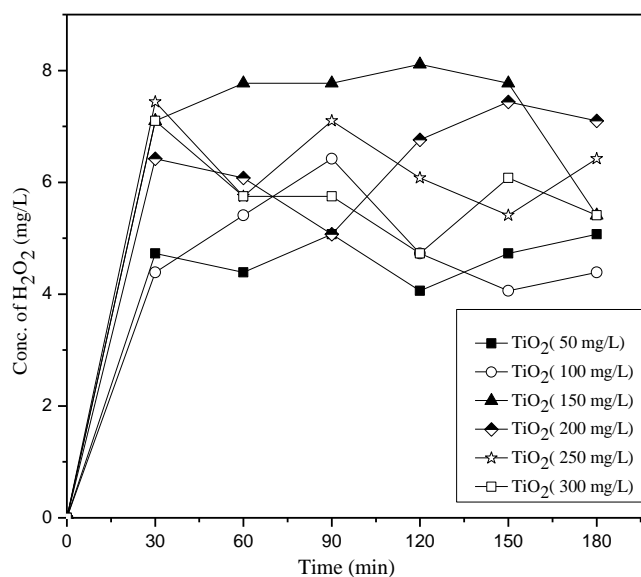**Figure 3a:** Effect of catalyst loading on the degradation of phenol

Figure3b: Effect of catalyst loading on the oscillation in the concentration of H_2O_2

Since the formation and decomposition of H_2O_2 are occurring in parallel all the time, optimization of catalyst loading with respect to H_2O_2 formation may not be reliable. In any case the maximum in the oscillation curve is high at higher loading of 0.20 and 0.25g/L. At catalyst dosage of 0.15 g/L, the H_2O_2 concentration remains steady for longer time and starts decreasing only after150 min.In this case the oscillation may set in later. This is consistent with earlier reported results on the unpredictability of H_2O_2 concentration at any point in the sono or photocatalysis. For these reasons the optimum loading of TiO_2 for phenol degradation is taken as the basis for further studies on the oscillation in the concentration of H_2O_2also.

3.2 Effect of concentration of substrate

The effect of concentration of phenol on the rate of photocatalytic degradation has been investigated earlier [12-14]. The degradation increases with increase in the concentration of phenol up to an optimum level beyond which it levels off or decreases slightly, due to saturation of the catalyst surface. The degradation

follows pseudo first order kinetics at lower concentration and zero order at later stage. However the effect of varying concentration of phenol on the fate of H_2O_2 in TiO_2 sonocatalysis has not been investigated so far. Hence this aspect is examined here. Asthe concentration of phenol increases the maximum in the oscillation curve of H_2O_2also increases (Fig. 4). The minimum also is relatively higher possibly because the rate of formation dominates rate of decomposition morefrequently.This may be due to the formation of more ˙OH radicals from phenol.
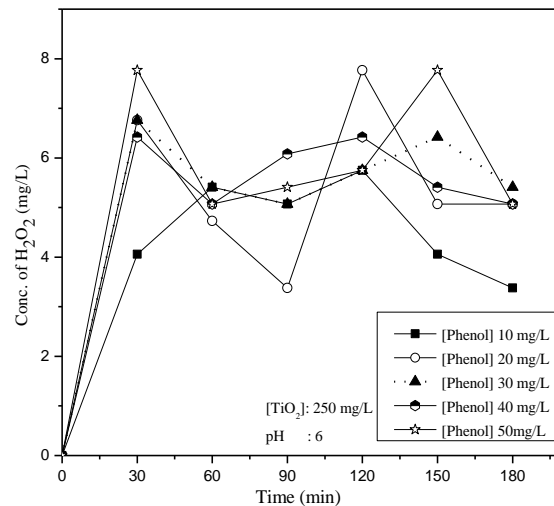

Figure 4: Effect of concentration of phenol on the oscillation in the concentration of H_2O_2

3.3 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 [11] have shown that the degradation is more efficient in the acidic region than in the alkaline region. In the case of TiO_2maximum degradation of phenol is observed at pH 6. The degradation continues to increase with time and eventually slows down at all pH. The pH effect is explained based on the point of zero charge (PZC) ofTiO_2 and corresponding change in the absorption characteristics. The effect of pH on the fate of $H_2O_2$is investigated and is shown in Fig. 5.
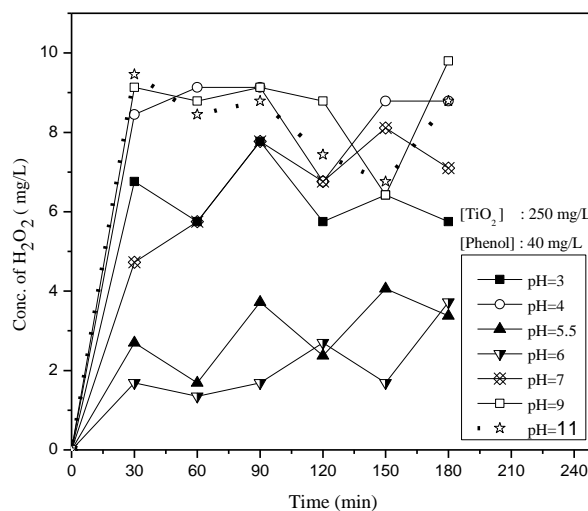

Figure 5: Effect of pH on the oscillation in the concentration of H_2O_2

At lower pH where the degradation of phenol is more, the net amount of H$_2$O$_2$ is relatively less. The oscillation occurs more frequently with lower concentration at both maxima as well as minima. This is probably because of the competition between phenol, various intermediates and H$_2$O$_2$itself for the reactive free radicals, resulting in increased degradation of phenol and decreased accumulation of H$_2$O$_2$. At higher pH, the interaction with phenol is less and the free radicals can interact among themselves to form more H$_2$O$_2$. This result in higher net concentration of H$_2$O$_2$.In order to decipher the effect of phenol and its decomposition products on the oscillation, the sonocatalytic decomposition of H$_2$O$_2$ on TiO$_2$ was investigated in the absence of phenolunder identical conditions (Fig. 6). 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.
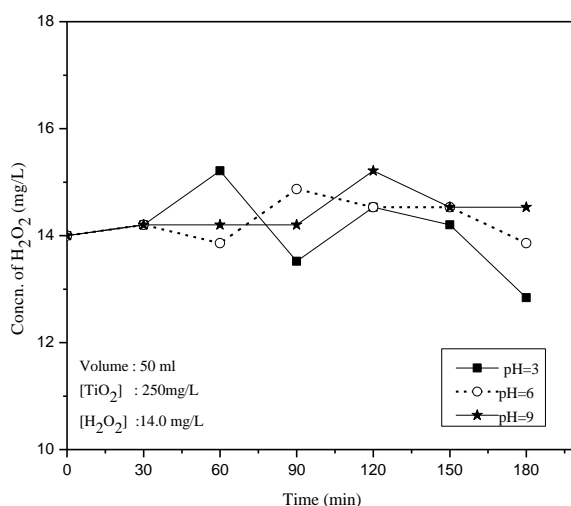

Figure6: Effect of pH on the fate of H$_2$O$_2$ during sonication in presence of TiO$_2$

3.4 Role of O$_2$ in the fate of H$_2$O$_2$

Presence of O$_2$ is essential for all AOPs which depend on the Reactive Oxygen Species. The degradation of phenol under sono and photocatalysis also has been proven to be inhibited in the absence of air/ O$_2$. The necessity of O$_2$ for the occurrence/propagation of oscillation is tested by deaerating the reaction system with N$_2$. The results are shown in Fig. 7.
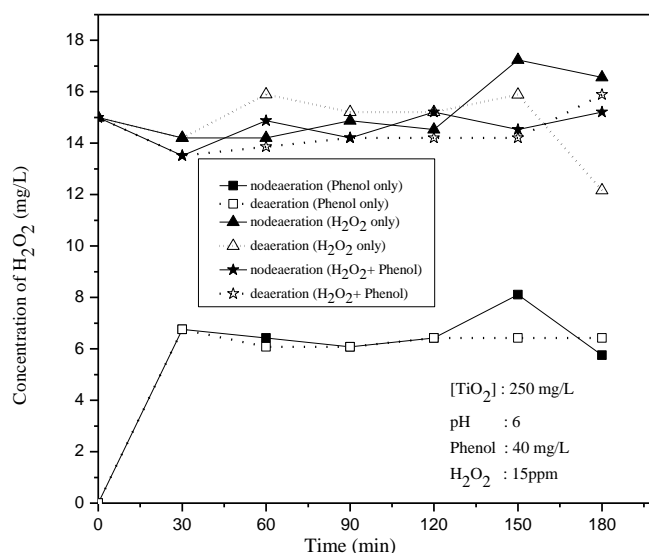

Figure7: Effect of deaeration on the oscillation in the concentration of H$_2$O$_2$

As stated earlier, small amount of $H_2O_2$is formed in sonocatalysis even in the absence of catalyst or phenol, possibly from sonolytic effect on water. The phenomenon of oscillation is observed even in the deaerated systems, though with much reduced maxima and minima in the concentration of H_2O_2, suggesting that once H_2O_2 is formed by whatever mechanism, subsequent decomposition and formation can take place even in the absence/reduced concentration of O_2. Here H_2O_2 itself can act as an electron acceptor andhole scavenger as follows:

$$H_2O_2 + e^- \quad \rightarrow \quad {}^{\cdot}OH + OH^- \quad (6)$$
$$H_2O_2 + {}^{\cdot}OH/h^+ \quad \rightarrow \quad HO_2{}^{\cdot}+ H_2O/H^+ \quad (7)$$

The $HO_2{}^{\cdot}$or${}^{\cdot}OH$ thus generated may also react on thesurface either to regenerate H_2O_2 or degrade or mineralize the pollutants.

3.5 General 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[17]. 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. Under ultrasonic irradiation, a series of thermal and photochemical reactions take place on the surface of composite TiO_2particles. The electron transport in the TiO_2 prevents the electron – hole recombination and increases the sonocatalytic activity.

The overall mechanism of H_2O_2 formation and decomposition under sonocatalytic conditions can be explained based on the formation and subsequent interaction of ${}^{\cdot}OH$ [13]. Recombination and a number of other reactions occur within the bubble as in reactions (8) and (9) following this primary radical generation as above.

$$
{}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad (8)
$$
$$
H^{\cdot}+ H_2O \rightarrow {}^{\cdot}OH + H_2 \quad (9)
$$
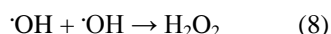
Subsequently H_2O_2 is formed as in reactions (2) – (4). The H_2O_2 thus formed decompose concurrently as in reactions (6) and (7) above.

IV.   CONCLUSION

Hydrogen peroxide formed during the sonocatalytic degradation of phenol in water in presence of semiconductor oxideTiO_2 undergoes concurrent formation and decomposition resulting in oscillation in its concentration. Various reaction parameters such as catalyst loading, substrate concentration, pH and presence of air/O_2 influence the phenomenon in general and the maxima and minima in the oscillation curve in particular. H_2O_2 plays a unique role in the process as acceptor of both electrons and holes. A general mechanism based on the observations is proposed and discussed.

V.   Acknowledgement

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