SUMMARY AND CONCLUSION

AOPs such as sono, photo and sonophoto catalysis for the purification of polluted water under ambient conditions involve the formation and participation of ROS like \( ^\cdot \text{OH}, \ \text{HO}_2^-, \ \text{O}_2^-, \ \text{H}_2\text{O}_2, \) etc. Among these, \( \text{H}_2\text{O}_2 \) is the most stable and is also a precursor for other reactive free radicals. The main objective of the current study was to investigate the fate of \( \text{H}_2\text{O}_2 \) formed during sono, photo and sonophoto catalytic processes. The net concentration of \( \text{H}_2\text{O}_2 \) measured in the system was not consistent with the rate of its generation. It is not reproducible either. The study is an investigation into the ‘missing’ of \( \text{H}_2\text{O}_2 \) from the system and its unusual behavior. The study also throws more light on the influence of naturally occurring contaminants such as various cations and anions on the efficiency of degradation of the pollutants and the fate of concurrently formed \( \text{H}_2\text{O}_2 \).

The semiconductor oxide catalyst used for the study was ZnO and the pollutant tested was phenol, which is one of the major chemical pollutants found in wastewater from petrochemical industries. The catalyst was characterized by standard wet analytical, adsorption and instrumentation techniques. The pollutant phenol was analyzed by UV-VIS spectrophotometry and the concentration of \( \text{H}_2\text{O}_2 \) was measured by standard iodometry. Various reaction parameters such as catalyst
dosage, pH, pollutant concentration, presence of contaminants, O₂, etc. were optimized for the degradation of the pollutant. The fate of H₂O₂ under each of the three AOPs is also closely monitored quantitatively.

Major findings of the study and the conclusions are as follows:

1) Semiconductor oxide mediated photocatalysis is an environment-friendly process for the removal of trace amounts of phenol from water. H₂O₂ is one of the stable intermediates formed during the degradation of phenol and it functions also as a precursor for other reactive free radicals. The concentration of H₂O₂ formed during the photocatalytic degradation of phenol cannot be quantitatively correlated with the phenol degradation. H₂O₂ undergoes concurrent decomposition resulting in ‘oscillation’ in its concentration. The concentration at which decomposition/formation overtakes one another is sensitive to the reaction conditions. Various parameters such as catalyst loading, substrate concentration, particle size, pH, externally added H₂O₂ and presence of air/O₂ influence this unique phenomenon of oscillation. The oscillation in the concentration of H₂O₂ continues for some more time even after the energy source is switched off, indicating the residual activity of the catalyst, i.e., ‘memory effect’. A reaction mechanism for the photocatalytic degradation of phenol and the oscillation phenomenon is proposed and discussed.

2) Sonication and sonocatalysis are also potential AOPs for the removal of toxic organic pollutants from water. However the efficiency of sonocatalytic process is much lower compared to
photocatalysis. Here also the intermediate formed during the degradation process, i.e., $\text{H}_2\text{O}_2$, undergoes concurrent decomposition resulting in oscillation in its concentration. The oscillation is influenced by various reaction parameters such as catalyst loading, substrate concentration, particle size, pH, externally added $\text{H}_2\text{O}_2$, presence of air/O$_2$, etc. $\text{H}_2\text{O}_2$ plays a unique role in the process as acceptor of both electrons and holes. Suitable mechanism for the process, taking various observations into consideration is proposed and discussed.

3) The basic mechanism of sonocatalysis involves the formation of ‘hotspot’ and sonoluminescence. US induced sonoluminescence makes sonocatalysis partially photocatalytic thereby opening the possibility of combining the two process i.e., sonophotocatalysis for enhanced efficiency. The sonophotocatalytic degradation of phenol in the concurrent presence of UV and US is more than the sum of the degradation under photocatalysis and sonocatalysis, which confirms the synergy. The oscillatory behavior of $\text{H}_2\text{O}_2$ observed in the case of sono and photo catalysis is less evident in sonophotocatalysis probably due to the accelerated rate of formation compared to decomposition. The net concentration of $\text{H}_2\text{O}_2$ in the system at any point of time is in the order; sono < photo < sonophoto. The reaction parameters which affect the concentration of $\text{H}_2\text{O}_2$ in the system are catalyst loading, substrate concentration, particle size of catalyst, pH, externally added $\text{H}_2\text{O}_2$, presence of air/O$_2$, etc. A mechanism taking into account the observations is proposed and discussed.
4) The impact of the presence of natural and man-made contaminants in water on the efficiency of the degradation process is also investigated in detail. It was observed that the inorganic salts likely to be present in water influence the rate of degradation and the behavior of insitu formed H$_2$O$_2$ under sono, photo and sonophoto catalysis. The effect of salts is dependent on the reaction time and concentration of the anions. Contrary to many earlier reports, current study shows that the inorganic salts enhance the sono, photo and sonophoto catalytic degradation of phenol. Various anions interact with the reactive $\cdot$OH radicals and respective radical anions are produced which cause the enhancement effect. Oscillation in the concentration of H$_2$O$_2$ is also influenced by the salts. But in this case there is no consistent pattern for the salt effect. The cations also influence sono, photo and sonophoto catalysis. However it is the anions in the salt that has more dominant role in deciding the salt effect. In short, identification of the contaminants in water is important in the design of appropriate and efficient treatment methods.

To sum up, ZnO mediated sono, photo and sonophoto catalytic degradation of phenol in water generates H$_2$O$_2$ as an intermediate as well as final product. The H$_2$O$_2$ thus formed undergoes concurrent decomposition resulting in oscillation in its concentration in sonocatalysis, weak oscillation/stabilization in photocatalysis and stabilization in the case of sonophotocatalysis. Once the concentration of H$_2$O$_2$ reaches a particular maximum, decomposition process starts dominating. Similarly the formation will start dominating, once a critical minimum is reached. H$_2$O$_2$
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is an important water soluble trace gas species in the atmosphere which can undergo various reactions in presence of photocatalytically active suspended particulate matter resulting in active free radicals. This can affect the chemistry of upper atmosphere, making the study of the fate of \( \text{H}_2\text{O}_2 \) in presence of light and sound relevant from the climate change angle as well.