

Influence of commonly occurring cations on the sono, photo and sonophoto catalytic decontamination of water

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Abstract: Sono, photo and sonophotocatalysis mediated by ZnO catalyst have been proven to be efficient methods for the removal of chemical and bacterial pollutants from water. Combination methods are often more efficient as in the case of sonophotocatalysis which is synergic. In this case, the efficiency is more than the sum of the respective sono- and photo- catalytic processes under otherwise identical conditions. The concentration of concurrently formed H_2O_2 increases and decreases periodically resulting in oscillatory behavior. Inorganic salts likely to be present in water influence the rate of degradation of the pollutant and the behavior of H_2O_2 . The effect of anions on the sono, photo and sonophotocatalytic degradation of phenol is dependent on the concentration of respective salts. Contrary to many earlier reports, current study shows that the anions and certain cations, enhance the sono, photo and sonophotocatalytic degradation of phenol. The rate of enhancement decreases with time and eventually becomes comparable to the rate without the presence of salts. The influence of various cations on the degradation of phenol and the fate of H_2O_2 is investigated under sono, photo and sonophotocatalysis. Almost all cations except Al^{3+} , irrespective of the nature of anions, enhance phenol degradation under sonocatalysis. In the case of photo and sonophotocatalysis, the effect of cations is relatively less to negligible. The effect of cations on the concurrently formed H_2O_2 as well as the oscillation phenomenon is inconsistent and unpredictable. The results are discussed and a tentative mechanism for the observation is proposed.

Keywords: Sonocatalysis, Photocatalysis, Sonophotocatalysis, Synergy, hydrogen peroxide, cations

I. Introduction

Advanced Oxidation Processes (AOPs) are efficient, environment-friendly techniques for the removal of chemical and bacterial pollutants from water. Relatively mild reaction conditions and proven ability to degrade several toxic refractory pollutants make them very attractive. Some of these AOPs include wet-air oxidation, radiolysis, cavitation, photolysis, photocatalysis, fenton chemistry, microwave degradation and electrochemical oxidation. They can be used either independently or in combination with other techniques in order to enhance the efficacy, economy and safety. Semiconductor-mediated sonocatalysis, photocatalysis and sonophotocatalysis have been promising with relatively higher rates of degradation for a variety of molecules [1-4]. Earlier studies from our laboratory [2] showed that sonophotocatalysis is synergic and the efficiency of the combination for the degradation of pollutants is more than the sum of individual photocatalysis and sonocatalysis.

The chemical effects of US in liquid include cavitation which consists of nucleation, growth and collapse of bubbles, resulting in localized supercritical condition such as high temperature, pressure, electrical discharges and plasma effects [5,6]. The gaseous contents of a collapsing cavity reach temperatures of approximately $5500^\circ C$ and the liquid immediately surrounding the cavity reaches up to $2100^\circ C$. The cavities thus serve the purpose of high energy micro reactors. The consequence of these extreme conditions is the cleavage of dissolved oxygen molecules and water molecules. The H^\bullet , OH^\bullet and O^\bullet radicals formed in the process will react with each other as well as with H_2O and O_2 during the rapid cooling phase giving HO_2^\bullet 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 pollutants.

In photocatalysis, photo excitation of the semiconductor oxide promotes valence band electrons to the conduction band thereby creating electron deficiency or hole in the valence band. Dioxygen provides a sink for conduction band electron forming superoxide $\cdot O_2^-$ which leads to the formation of hydroperoxide HO_2^\bullet . Holes in the valence band can react with water molecules or hydroxide anion to form OH radicals. These reactive species can interact with the pollutants leading to their degradation and possibly mineralization. The mechanisms of photocatalytic and sonocatalytic reactions are similar and this has opened up the possibility of combining the techniques for enhancing the degradation of organic pollutants in water.

The most widely studied catalyst in sono-, photo- and sonophotocatalysis is TiO₂ in view of its favorable physico-chemical properties, low cost, easy availability, high stability with respect to photocorrosion and chemical corrosion, and low toxicity. Another semiconductor oxide ZnO with band-gap energy of ~3.2 eV has properties comparable to those of TiO₂ and is capable of absorbing a larger fraction of the solar spectrum [7]. Hence it is more active in the visible region for the photocatalytic decontamination of water [8, 9]. The comparatively lower light-scattering effect of ZnO due to its lower refractive index (ZnO: 2.0, TiO₂: 2.5–2.7) also favours better photocatalytic efficiency. In spite of these advantages, ZnO has not received due attention as an effective environmental photocatalyst, probably due to its instability or photocorrosion under acidic conditions.

We have earlier reported the sono, photo and sonophotocatalytic degradation of water pollutants in presence of semiconductor oxides and the fate of concurrently formed H₂O₂ [2, 10]. Unlike in the case of the pollutants which undergo progressive degradation with time and eventual mineralization, H₂O₂ formed during the process does not increase correspondingly and is undergoing concurrent formation and decomposition resulting in oscillation in its concentration. Various reaction parameters influence the oscillatory behavior though the same cannot be quantitatively correlated. Further to our earlier investigations on the effect of various anions in AOPs, the influence of a number of cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺) which are likely to be present in water on the ZnO mediated sono, photo and sonophotocatalytic degradation of phenol and the oscillation in the concentration of simultaneously formed H₂O₂ is undertaken in the current study.

II. Materials and methods

ZnO (99.5%) used in the study was supplied by Merck India Limited. The surface area, as determined by the BET method is ~ 12 m²/g. The consistency of the physicochemical characteristics of ZnO used in the study with those reported in literature was confirmed by X-ray diffractogram (XRD) and Scanning Electron Microscopy (SEM) measurements. Phenol AnalaR Grade (99.5% purity) and H₂O₂ (30.0% w/v) from Qualigen (India) were used as such without further purification. All other chemicals were of AnalaR Grade or equivalent. Water distilled twice was used in all the experiments. The sonocatalytic, photocatalytic and sonophotocatalytic experiments were performed as reported earlier [2]. The phenol degradation was followed by periodic sampling and analyzing by UV-VIS spectroscopy (500 nm). Adsorption and mineralisation studies were made using standard techniques. Concentration of H₂O₂ was determined by iodometry [10].

III. Results and discussion

Preliminary studies on the degradation of phenol in water in the presence of ZnO showed that the catalyst and an energy source are essential to effect reasonable degradation. The degradation is more facile in the presence of UV light (photocatalysis) compared to US irradiation (sonocatalysis). The sonophotocatalytic degradation of phenol in the concurrent presence of UV, US and ZnO is more than the sum of the degradation under photocatalysis and sonocatalysis (Figure 1), which confirms the synergy reported in similar instances earlier [3,5]. The synergy index is calculated using equation (1) [11]:

$$\text{Synergy index} = R_{\text{US+UV}} / (R_{\text{US}} + R_{\text{UV}}) \quad (1)$$

where R_{US}, R_{UV} and R_{US+UV} are the sono, photo and sonophoto catalytic degradation rates respectively. The synergy index thus calculated for ZnO is 1.25.

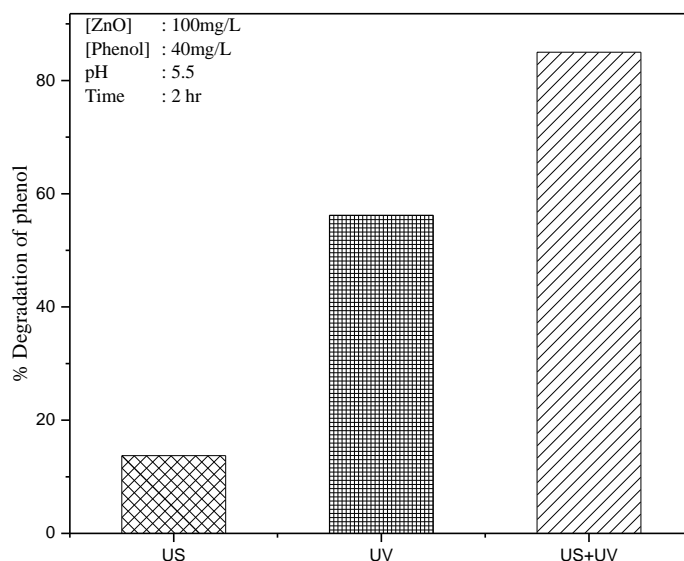


Figure 1. Sono-, photo- and sonophotocatalytic degradation of phenol in the presence of ZnO.

The optimum catalyst loading, as determined in the case of sono, photo and sonophotocatalysis from a series of experiments, is 100 mg/L. The degradation follows concentration-dependent variable kinetics, with pseudo first order at lower concentration and zero order at higher concentration. At the optimized catalyst dosage, optimum reaction rate was achieved at phenol concentration of 40 mg/L. pH studies showed that the natural pH of the reaction suspension, i.e. 5.5 is the optimum for sono, photo and sonophotocatalysis. Hence all further studies on the influence of various ions on the sono, photo and sonophotocatalytic degradation of phenol and the concurrently formed H_2O_2 were carried out using these optimized reaction conditions.

The effect of various anions on the degradation of phenol under sono, photo and sonophotocatalysis is shown in figure. 2

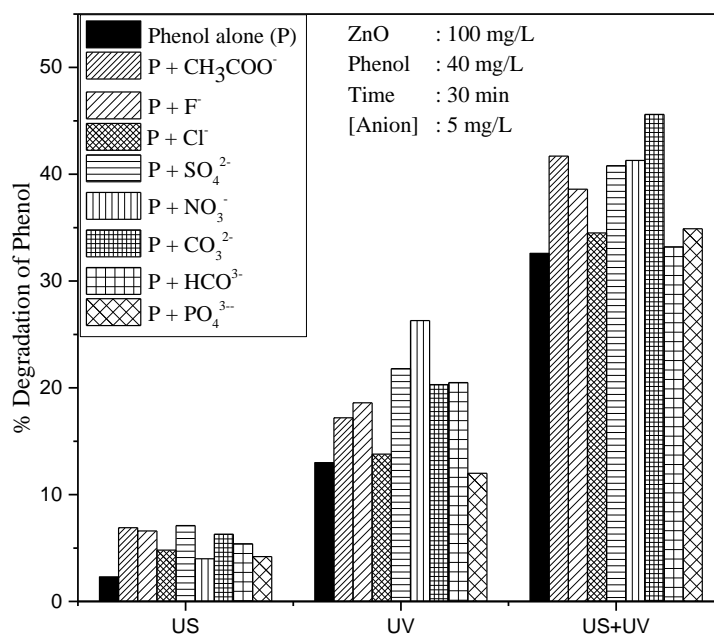


Figure 2. Effect of anions on the sono, photo and sonophotocatalytic degradation of phenol

Surprisingly, all the anions enhance the sonocatalytic degradation of phenol in the beginning of the reaction and at lower concentration. In photocatalysis, except PO_4^{3-} all other anions enhance the degradation by varying degrees. But in the case of sonophotocatalysis, the anions Cl^- , HCO_3^- and PO_4^{3-} have practically no effect while others enhance the degradation. This is contrary to the inhibition to photocatalytic degradation of organics caused by anions, as reported by many research groups [12, 13]. Reduced availability of catalytic surface sites for adsorption of the substrate due to competition from the anions is often cited as the reason for the inhibition. The anions are also known to scavenge the ROS, especially $\cdot\text{OH}$, which also could have caused the inhibition. However in the present instance, the role is reversed and at least some of the anions are accelerating the degradation of phenol. The enhancement in the case of sono/photo/sonophoto catalysis is explained partially based on the formation of reactive radical species such as F^- , $\text{CO}_3^{\cdot-}$, $\text{SO}_4^{\cdot-}$ etc from respective anions by interaction with the $\cdot\text{OH}$ on the surface of cavitation bubbles, on the surface of the catalyst or in the bulk, individually or in suitable combination [14]. These species, though less reactive than the $\cdot\text{OH}$, are more abundant and do not get deactivated easily as in the case of $\cdot\text{OH}$ radicals.

The results of the investigations on the anion effect in various AOPs are being reported separately from our research group. In all these cases the cation was the same, i.e. Na^+ . At the same time, understanding the specific effect by the cation also is important in the design of suitable AOP system for wastewater treatment. In this context, the effect of various cations such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} on the sono, photo and sonophotocatalytic degradation of phenol is carried out. The anions in these cases were NO_3^- , SO_4^{2-} and Cl^- . For each anion, the effect of various cations on the degradation is investigated. The results are plotted in figures 3 (Nitrate), 4 (Sulphate) and 5 (Chloride) respectively.

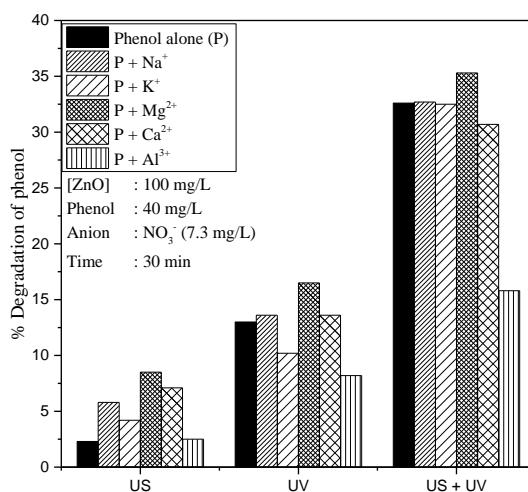


Figure 3. Effect of various cations (anion: nitrate) on the sono, photo and sonophotocatalytic degradation of phenol

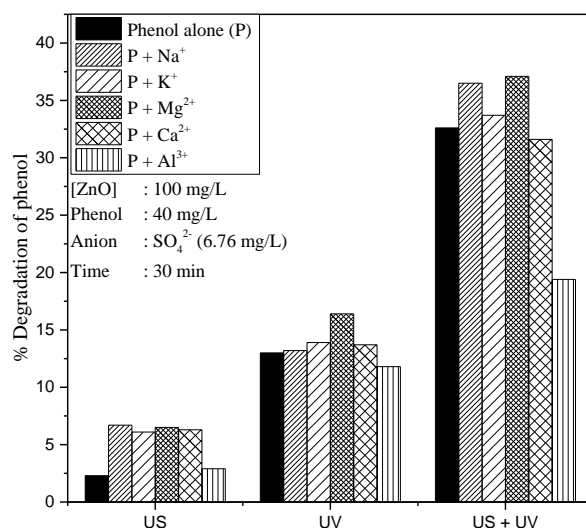


Figure 4. Effect of various cations (anion: sulphate) on the sono, photo and sonophotocatalytic degradation of phenol

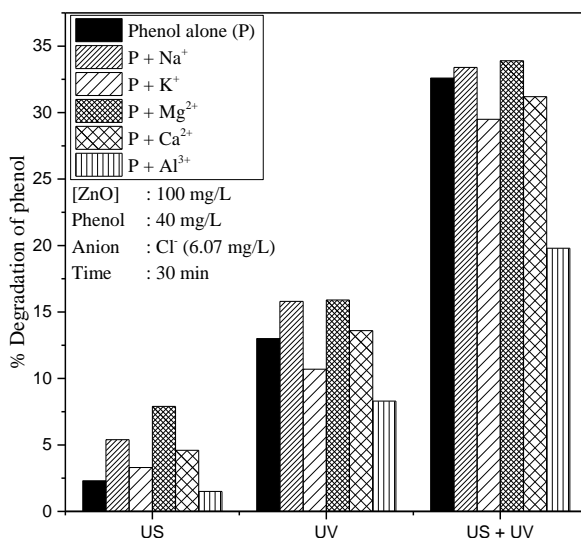


Figure 5. Effect of various cations (anion: chloride) on the sono, photo and sonophotocatalytic degradation of phenol

In the case of sonocatalysis all cations except Al³⁺ enhances phenol degradation, even though the degree of enhancement varies with different anions. In the case of NO₃⁻ anion, the order of enhancement for various cations is Al³⁺ < K⁺ < Ca²⁺ < Na⁺ < Mg²⁺. In the case of sulphate as the anion, the enhancement in presence of cations except Al³⁺ remains more or less same in all cases. Incidentally sulphate anions exhibit maximum enhancement for the degradation of phenol. In this case the enhancement is in the order Al³⁺ < K⁺ ≈ Ca²⁺ ≈ Na⁺ ≈ Mg²⁺. When the anion is chloride, the enhancement in presence of cations still holds, though the order of efficiency is different, i.e. Al³⁺ < K⁺ < Ca²⁺ < Na⁺ < Mg²⁺. The identical trend in presence of the cations irrespective of the difference in the anions, in the case of NO₃⁻ and Cl⁻, and the significantly different trend when SO₄²⁻ is the anion indicate that it is difficult to isolate and compare the effect of cations when the anions are different.

In photocatalysis, in presence of Al³⁺ and K⁺ the phenol degradation is inhibited when the anion is Cl⁻ or NO₃⁻. Maximum enhancement is obtained in the case of Mg²⁺ and Na⁺. In this case also, the trend is different

in presence of sulphate anion. In this case Mg^{2+} has clear enhancing effect while all other cations have only negligible effect. Even the inhibitory effect of Al^{3+} and K^+ also is insignificant in this case.

In sonophotocatalysis the synergistic effect is not affected in presence of various cations. Except for Al^{3+} other cations have no significant effect on the degradation. The trend remains more or less the same as in the case of photocatalysis, including the consistent enhancing effect by Mg^{2+} .

Our earlier studies have shown that the effect of various salts on the AOP degradation of pollutants depends on the reaction time. Hence the influence of cation effect at another reaction time, i.e. 60 minutes, on the degradation is tested, keeping SO_4^{2-} as the anion. The results are presented in figure.6. The results show that unlike in the case of anions, extended reaction time does not modify the initial effect by cations on the degradation.

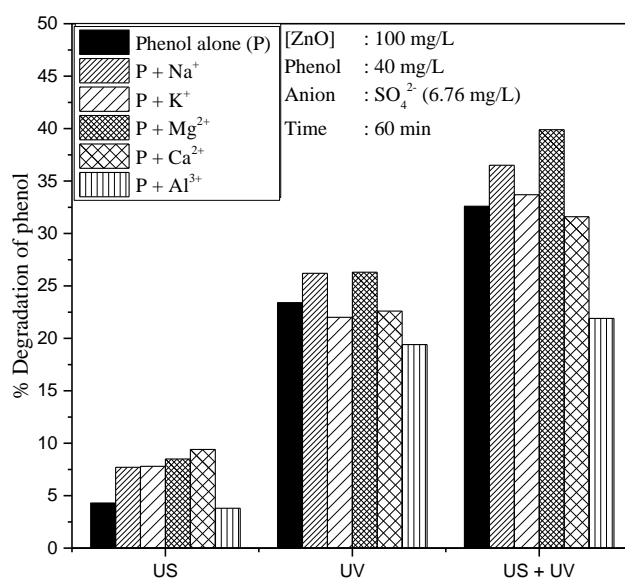


Figure 6. Effect of various cationic sulphates on the sono, photo and sonophotocatalytic degradation of phenol

One possible explanation for the effect of cations on the rate of degradation of organics in the presence of catalysts is their adsorption/layer formation on the surface. The layer formation may inhibit or promote the adsorption of the substrate and subsequent activation in presence of UV/US/(US+UV). In this case, the size of the cation may have a role, higher the size, greater the surface coverage and less the degradation of the substrate. However, the results do not show any specific trend based on the cationic size suggesting that the effect of cations is not that simple or straightforward.

In order to verify whether the effect of cations is related to their blocking the active surface sites, the adsorption of phenol in presence of these cations was measured. The results are plotted in Figure 7.

From the figure it is clear that phenol adsorption is the least in presence of Al^{3+} cations when the anion is SO_4^{2-} . The adsorption is inhibited to the maximum by $Al_2(SO_4)_3$ followed by $NaCl$, KCl and $MgSO_4$. However, the adsorption is enhanced by $NaNO_3$, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ while $Al(NO_3)_3$ and KNO_3 do not affect. $CaSO_4$ enhances the adsorption significantly. Once again there is no direct or consistent correlation between the nature of the cation and the adsorption of phenol. If at all there is some kind of correlation, it is between the nature of the anions and the adsorption/degradation.

Previous studies have reported that sonocatalytic and photocatalytic reactions are sensitive to the presence of anions [15, 16]. Seymour and Gupta [15] observed $NaCl$ induced enhancement in sonocatalytic degradation of organics using 20 kHz US. It is also reported that the presence of massive amounts of Cl^- ions inhibit photocatalytic degradation [17]. The addition of salt increases the ionic strength of the aqueous phase. In the case of sonocatalysis,

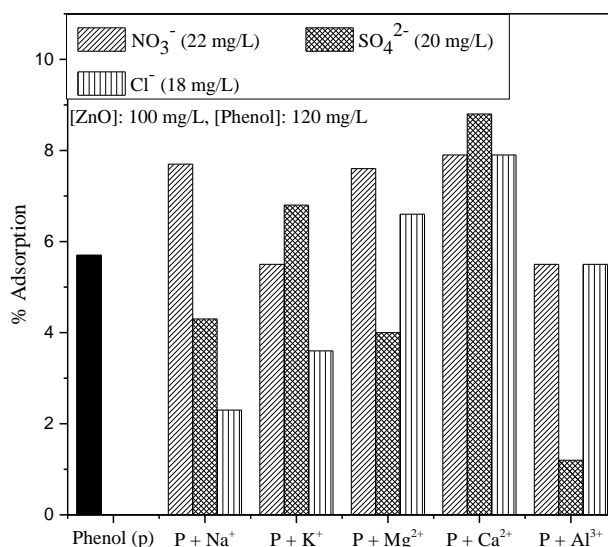


Figure 7. Effect of cations on the adsorption of phenol in presence of Nitrate, Sulphate and Chloride anions

this is expected to drive the organic pollutants towards the bubble-bulk interface where the majority of the sonodegradation takes place [18]. The increase in surface tension can affect the nucleation process and the cavitation threshold. The presence of salt will also increase the partitioning of the organic species upon cavitation implosion. Thus it was expected that the interfacial concentration of the pollutants would increase which could enhance the overall degradation rate. However, these explanations have to be selectively applied and cannot be generalized. Also it may not be quite appropriate to isolate the effects as anionic or cationic since both cations and anions do influence the degradation of the pollutant, either complementarily or conversely.

The effect of the above cations on the concurrently formed H₂O₂ under sono, photo and sonophotocatalysis is also examined keeping nitrate as the typical anion (figures 8-10). In particular, the effect on the phenomenon of oscillation is critically examined. There is no consistent trend in this case as well. However, the net concentration of H₂O₂ is more in all cases, thereby demonstrating a correlation with the enhanced rate of phenol degradation. The amount of H₂O₂ is relatively less in presence of Al³⁺ cation which inhibits phenol degradation. In the case of sonophotocatalysis the trend is not strictly followed probably due to the interplay of a number of factors and formation of multitude of free radicals which interact in a variety of ways. Hence it may be tentatively inferred that the cations tested here inhibits the competitive decomposition of H₂O₂ resulting in higher amounts of the peroxide. Hence the simultaneous formation process in the oscillation phenomenon dominates and the net H₂O₂ is more. Even under well defined experimental conditions, oscillation is not amenable to any clear interpretation due to the complexity of the system consisting of a number of reactive free radicals, concurrent formation and decomposition of H₂O₂ and the creation of a series of intermediates, many of them competing with each other. However, the enhancing effect of the cations, except Al³⁺, on the sono, photo and sonophotocatalytic degradation of phenol is evident in the case of H₂O₂ also.

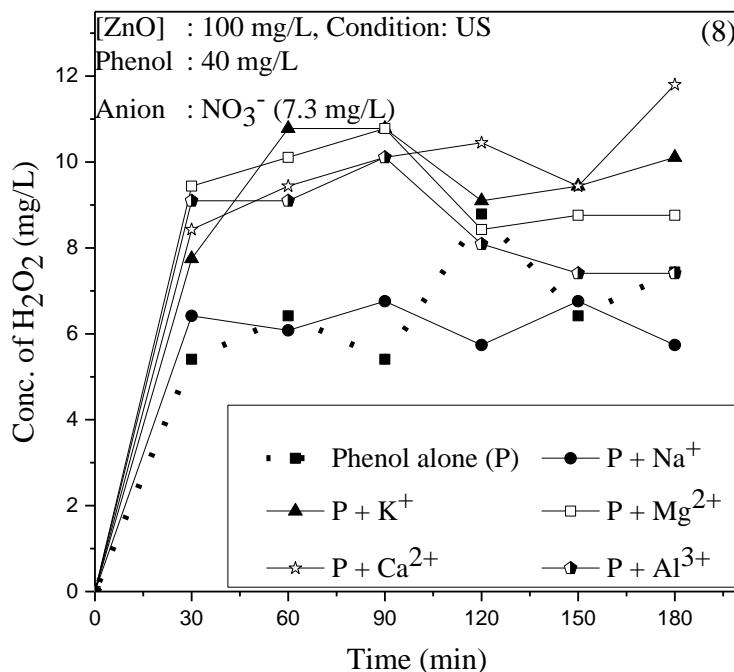


Figure 8. Effect of various cations on the oscillation in the concentration of H₂O₂ under sono catalysis (Anion: nitrate)

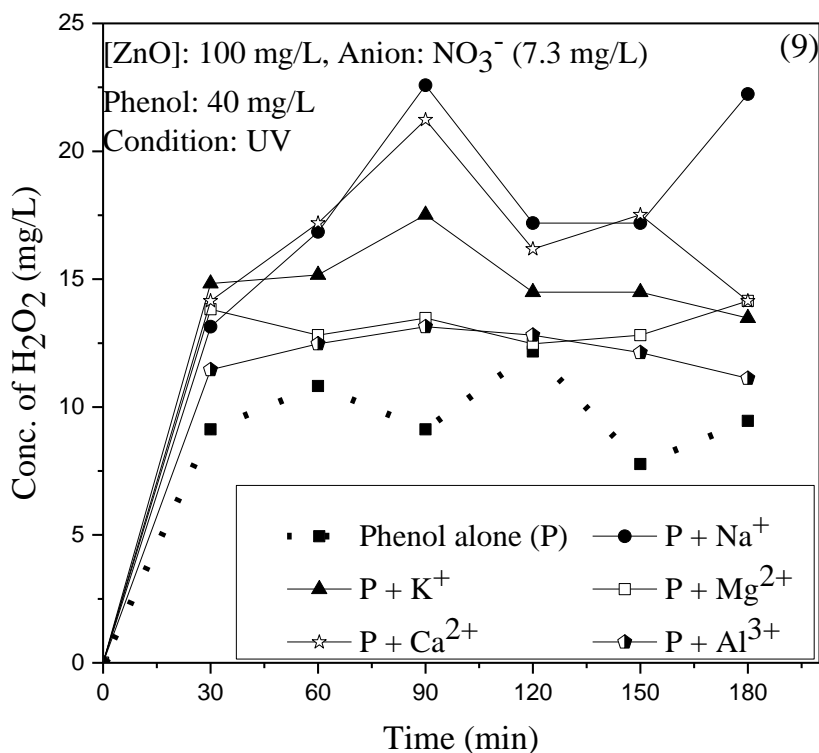


Figure 9. Effect of various cations on the oscillation in the concentration of H₂O₂ under photo catalysis (Anion: nitrate)

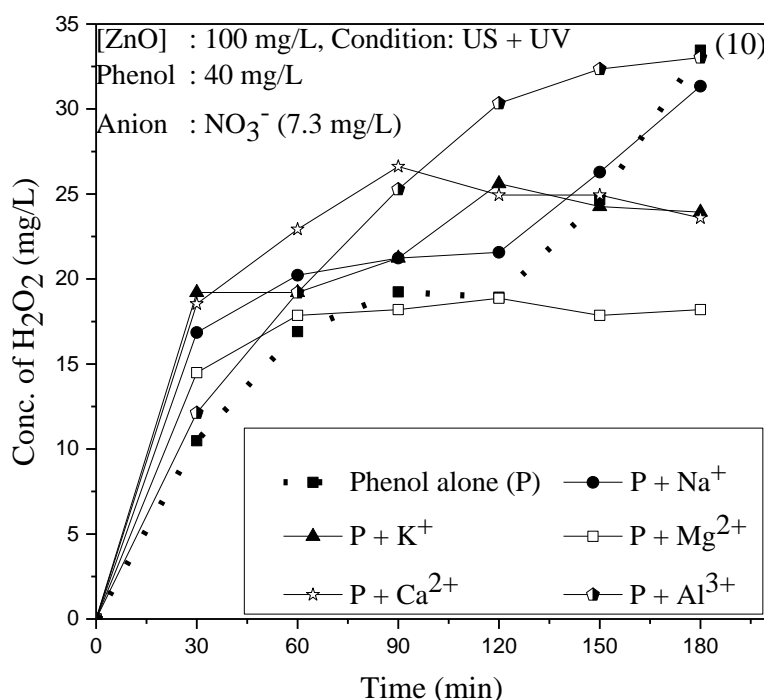
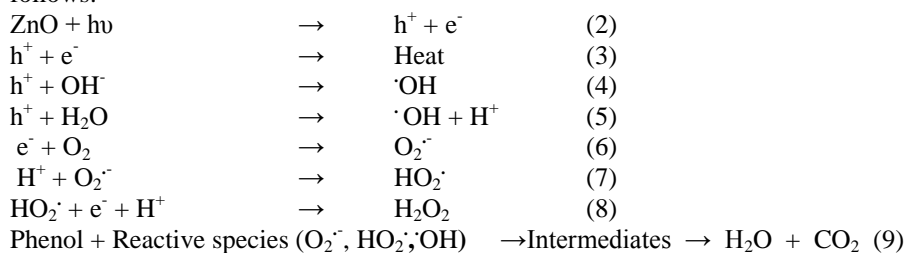


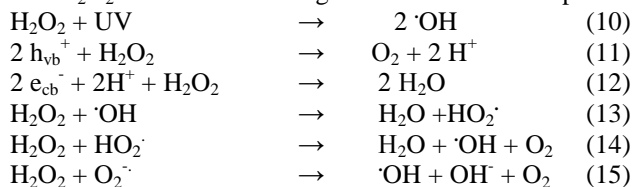
Figure 10. Effect of various cations on the oscillation in the concentration of H₂O₂ under sonophoto catalysis (Anion: nitrate)

IV. General mechanism

The basic mechanism of ZnO mediated sono, photo and sonophotocatalytic degradation of phenol is as follows:



The H₂O₂ thus formed undergoes concurrent decomposition by a series of interactions as follows:



Thus, the same free radicals can contribute to the formation and decomposition of H₂O₂ depending on the conditions.

Anions act as radical scavengers and thus in the presence of anions, the relative abundance of OH radicals is decreasing very fast. But the radical anions produced as a result of interaction between ·OH radical and anions can also effect the degradation of organics. Unlike in the case of ·OH radicals which get deactivated by a number of competing reactions, the radical anions are available only for the degradation of the anions. This leads to enhancement in the degradation. The effect of cations is even more complex and cannot be explained in general. Hence the reaction parameters have to be optimized for every type of effluent water depending on the nature of salt contaminants for optimum efficiency in sono, photo and sonophotocatalysis.

V. Conclusion

Sono, photo and sonophotocatalysis mediated by ZnO catalyst have been proven to be efficient methods for the removal of chemical and bacterial pollutants from water. Combination methods are often more efficient as in the case of sonophotocatalytic degradation of phenol which is synergic. In this case, the efficiency is more than the sum of the respective sono- and photocatalytic processes under otherwise identical conditions. The concentration of concurrently formed H₂O₂ increases and decreases periodically, resulting in oscillatory behavior. Inorganic salts likely to be present in water influence the rate of degradation of the pollutant and the behavior of H₂O₂. The effect of anions on the sono, photo and sonophotocatalytic degradation of organic pollutants like phenol is dependent on the concentration of respective salts. Contrary to many earlier reports, current study shows that the anions and certain cations, enhance the sono, photo and sonophotocatalytic degradation of phenol. The rate of enhancement decreases and eventually it becomes comparable to the rate without the presence of salts. The influence of various cations on the degradation of phenol and the fate of H₂O₂ is investigated under sono, photo and sonophotocatalysis. Almost all cations except Al³⁺, irrespective of the nature of anions, enhance phenol degradation under sonocatalysis. In the case of photo and sonophotocatalysis, the effect of cations is negligible. The effect of cations on the concurrently formed H₂O₂ as well as the oscillation phenomenon is inconsistent and unpredictable. The results are discussed and a tentative mechanism for the observation is proposed.

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