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Sono-, photo- and sonophotocatalytic decontamination of organic pollutants in water: studies on the lack of correlation between pollutant degradation and concurrently formed H_2O_2

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The degradation of trace amounts of phenol in water is studied under sono-, photo- and sonophotocatalytic conditions using ZnO as a catalyst. Sonophotocatalytic degradation is more than the sum of the respective sono- and photocatalytic degradation under otherwise identical conditions, indicating synergistic effect. The degradation proceeds through many intermediates and ultimately the parent compound is mineralized. The concentration of concurrently formed H_2O_2 increases and decreases periodically resulting in an oscillatory behaviour. The oscillation is more pronounced in sonocatalysis in which the degradation of phenol and corresponding formation of H_2O_2 are slower. In photocatalysis and sonophotocatalysis, where the degradation is faster, the amount of H_2O_2 is relatively more and the oscillation becomes weaker and tends towards stabilization. However, in all cases the degradation of phenol continues unabated until the mineralization is complete. The stabilized concentration of H_2O_2 is much less than the expected amount based on the degradation of the organic pollutant. Probable causes for the phenomena are discussed.

Keywords: Hydrogen peroxide, phenol, photocatalysis, sonocatalysis, zinc oxide.

ADVANCED oxidation processes (AOPs) based on the generation of highly reactive $^{\bullet}OH$ radicals which can attack the target molecules and mineralize them eventually to harmless CO_2, water and salts have been widely studied as viable candidates for the removal of chemical and bacterial pollutants from water. Some of these AOPs include wet-air oxidation, radiolysis, cavitation, photolysis, photocatalysis, fenton chemistry and electrochemical oxidation. They can be used either independently or in combination with other techniques in order to enhance the efficacy, economy and safety. In this context semiconductor-mediated sonocatalysis, photocatalysis and sonophotocatalysis have been promising with relatively higher rates of degradation for a variety of molecules[1–12]. The expected advantage of sonophotocatalysis is the

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*For correspondence. (e-mail: epyesodharan@gmail.com) synergy between photocatalysis and sonochemistry resulting in enhanced efficiency of the combined process. Relatively mild reaction conditions and proven ability to degrade several toxic refractory pollutants also make the process attractive. But large-scale application of this hybrid technique is hampered at least partially due to high cost and lack of suitable design strategies associated with the sonochemical reactors[10]. The status of sonophotocatalytic reactors and potential development needs were discussed in detail by Gogate and coworkers[8,10–12].

The most widely studied catalyst in sono-, photo- and sonophotocatalysis is TiO_2 in view of its favourable physico-chemical properties, low cost, easy availability, high stability with respect to photocorrosion and chemical corrosion, and low toxicity. However, TiO_2 has a wide band gap (~3.2 eV) and can absorb light only below 400 nm, which is in the UV range that constitutes less than 5% of sunlight. Many studies on improving the photocatalytic efficiency of TiO_2 by techniques such as dye sensitization, semiconductor coupling, impurity doping, use of coordination metal complexes, noble metal (Pt, Pd, Au, Ag, etc.) deposition, use of Fenton reagent and H_2O_2 have been reported[6–9]. The enhancement is attributed partially to the increased light absorption and inhibition of the recombination of electron–hole pair[13,14]. Another semiconductor with potential sono/photo catalytic applications is ZnO with properties comparable to those of TiO_2. Though both of them have comparable band-gap energy (~3.2 eV), in practice, ZnO is capable of absorbing a larger fraction of the solar spectrum[15] and hence is more active in the visible region for the photocatalytic decontamination of water[16–19]. The comparatively lower light-scattering effect of ZnO due to its lower refractive index (ZnO: 2.0, TiO_2: 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 which may be due to its instability or photocorrosion under acidic conditions.

Our earlier studies revealed that ZnO can be used as an effective catalyst for the degradation of certain organic pollutants in water using sunlight as the source of energy[17,20]. We have also studied the sono-, photo- and sonophotocatalytic degradation of phenol on ZnO and the synergy of the hybrid technique was demonstrated[4]. In the present communication the study is extended and the fate of H_2O_2 formed in ZnO-mediated sono-, photo- and sonophotocatalytic systems is examined using phenol as the test pollutant. Phenol is chosen as the candidate pollutant because it is rated as one of the most common and at the same time toxic organic pollutants in wastewater. The treatment of phenol-contaminated wastewater by hybrid techniques has been the subject of many studies and the findings are discussed exhaustively in recent reviews[5,8,9,11,12]. Addition of H_2O_2 enhances the efficacy of the process which is attributed to the increased availability of hydroxyl radicals formed by its dissociation[5,12]. At the same time, the H_2O_2 itself is formed primarily from the $^\bullet OH$ radicals which are generated in AOPs such as sono-, photo- and sonophotocatalysis[21–24]. Thus H_2O_2 functions as a reactant, intermediate and/or the end-product and the $^\bullet OH$ radicals serve at least partially as the creator and destroyer of H_2O_2. However, the fate of H_2O_2 in sono-, photo- or sonophotocatalytic systems has not received due attention since the focus has always been on the removal of the pollutant and purification of water. In the present work, the role and fate of H_2O_2 formed during the sono-, photo- and sonophotocatalytic degradation of phenol in water is studied in detail.

ZnO (99.5% purity, BET surface area 12 m^2/g) used in the study (Merck India Limited) was characterized by particle size, scanning electron microscopy (SEM), X-ray diffraction (XRD) and reflectance spectroscopy. Phenol AnalaR Grade (99.5% purity) from Qualigen (India) was used as such without further purification. All other chemicals were of AnalaR Grade or equivalent. Doubly distilled water was used in all experiments. The sono-, photo- and sonophotocatalytic experiments were performed as follows[4,25].

Specified quantity of the catalyst was suspended in phenol solution of desired concentration and kept under agitation using a magnetic stirrer. In the case of ultrasound (US) irradiation experiments, sonication was sufficient to ensure adequate mixing of the suspension. Additional mechanical mixing did not make any notable consistent difference in the US reaction rate. Hence mixing by sonication alone was chosen for all US and (US + UV) experiments. The reactor used in all experiments was a cylindrical Pyrex vessel of 250 ml capacity. In photocatalytic experiments, the reactor was placed in a glass vessel of 500 ml capacity through which water from a thermostat at the required temperature was circulated. A high-intensity UV lamp (400 W medium pressure mercury vapour quartz lamp) mounted above was used as the UV irradiation source. In the case of sonocatalytic and sonophotocatalytic experiments, ultrasonic bath was used as the source of US. The ultrasonic bath was operated at 40 kHz and power of 100 W. Water from the sonicator was continuously replaced by circulation from a thermostat maintained at the required temperature. The position of the reactor in the ultrasonic bath was always kept the same. Unless otherwise mentioned, the reaction temperature was maintained at $29 \pm 1°C$. At periodic intervals samples were drawn, the suspended catalyst particles were removed by centrifugation and the concentration of phenol left behind was analysed by spectrophotometry. The phenol was converted into coloured antipyrene dye by reaction with 4-amino antipyrene in the presence of potassium ferricyanide at pH 7.9 ± 0.1. The concentration of the dye was measured at 500 nm and correlated to the concentration of phenol. Sample from reaction system kept in the dark under exactly identical conditions but without UV or US irradiation was used as the reference.

H_2O_2 was determined by iodometry after removing the suspended particles from the sample by centrifugation. Mineralization of phenol was identified by confirming the evolution of CO_2 and determination of the total organic carbon (TOC) content using TOC analyzer (model Elementar Analysensysteme GmbH).

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 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 experiments earlier[4,9].

Small quantity of phenol degraded in the presence of US even in the absence of catalysts. Sonolysis of water produces extreme temperature and pressure conditions capable of generating free radicals $H^\bullet$ and $OH^\bullet$, which can lead to other reactive oxygen species (ROS)[26]. They interact with phenol resulting in eventual mineralization and formation of H_2O_2 as follows

$$H_2O \xrightarrow{>>>} H^\bullet + {}^\bullet OH, \qquad >>> \text{ refers to US} \tag{1}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet, \tag{2}$$

$$\text{ROS } ({}^\bullet OH,\ HO_2^\bullet, \text{ etc.}) + \text{phenol} \rightarrow \text{intermediates} + H_2O_2 \rightarrow H_2O_2 + H_2O + CO_2, \tag{3}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2, \tag{4}$$

$$2\ {}^\bullet OH \rightarrow H_2O_2. \tag{5}$$

The mineralization of phenol in photo- and sonophotocatalysis is verified by the absence of TOC after phenol was completely degraded and disappeared from the system. However, in sonocatalytic experiments the degradation took much longer periods and hence the mineralization could not be confirmed by TOC measurements. In this case also, it is logical to assume that the phenol disappearing from the system is eventually getting mineralized. The net TOC present in the system under identical conditions in sono-, photo- and sonophotocatalysis after 2 h of irradiation follows the order (US + UV) < UV << US, thereby reiterating the comparative mineralization efficiency of the three processes. The fate of concurrently formed H_2O_2 is shown in Figure 2.

The catalyst loading for optimum degradation of phenol has been experimentally determined for sono-, photo- and sonophotocatalysis respectively, as shown in Figure 3. The optimum loading is slightly higher at 100 mg/l in sonophotocatalysis compared to sono- and photocatalysis. In all three cases, the degradation increases with increase in catalyst loading and reaches an optimum range.

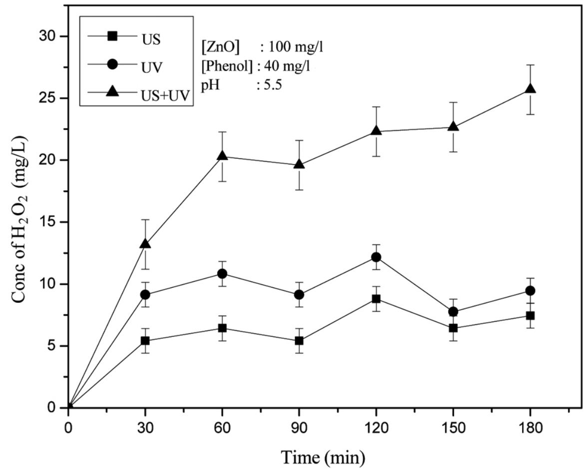

Figure 2. Concentration of H_2O_2 during sono-, photo- and sonophotocatalytic degradation of phenol in the presence of ZnO.

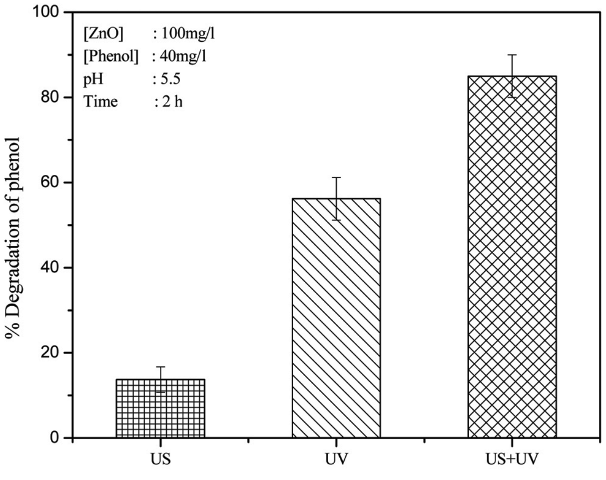

Figure 1. Sono-, photo- and sonophotocatalytic degradation of phenol in the presence of ZnO.

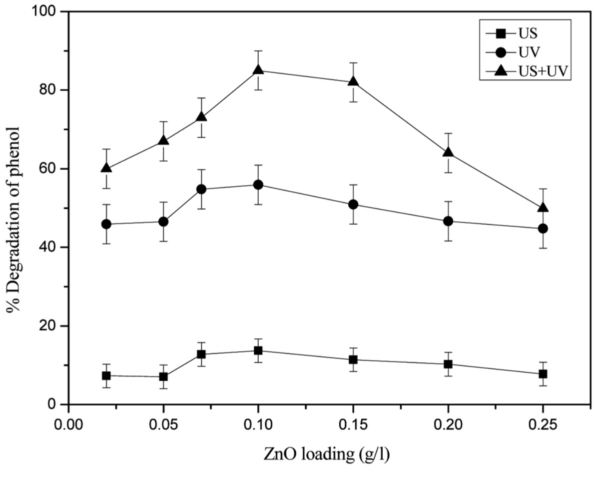

Figure 3. Effect of catalyst loading on sono-, photo- and sonophotocatalytic degradation of phenol in the presence of ZnO.

Beyond this optimum, the degradation slows down and thereafter remains more or less steady or even decreases. The enhanced degradation efficiency is probably due to increased number of adsorption sites and more effective interaction with the irradiation which lead to higher number of reactive hydroxyl radicals. In the case of photo- and sonophotocatalysis, any further increase in catalyst concentration beyond the optimum will only result in light scattering and reduced passage of light through the sample. Hence no further increase in degradation is observed. Another reason may be the aggregation of catalyst particles causing decrease in the number of available active surface sites. The particles cannot be fully and effectively suspended beyond a particular loading in a particular reactor, which also leads to suboptimal penetration of irradiation and reduced adsorption of the substrate on the surface. This can also result in stabilization or even decrease in the degradation after the optimum catalyst dosage. In the case of sonophotocatalysis, the decrease in degradation with increase in catalyst loading beyond the optimum is more pronounced compared to photocatalysis. However, the optimum loading and the trend remain fairly the same suggesting that US-induced increase in the rate of photocatalysis results at least partly from the increase in light absorbed by the reaction system. This leads to higher concentration of active species. At higher catalyst loading when filtering and/or scattering of light becomes more prominent, the amount of photoproduced active species does not increase further.

The optimum quantity of ZnO is in the order sonophotocatalysis > sonocatalysis ≥ photocatalysis. The higher optimum loading in sono- and sonophotocatalysis may be due to the deagglomeration of the aggregate catalyst particles by US, which can bring more surface sites in contact with the irradiation as well as the pollutant molecules. However, at higher ZnO concentrated suspension, the working volume of the slurry becomes low and light cannot penetrate into the optically dense medium[27]. Consequently, deagglomeration may not lead to any extra absorption of light as the zone of action of light can be different from the zone of action of US. Hence any further enhancement in degradation in sonophotocatalysis beyond the optimum catalyst loading for photocatalysis is due to the production of hydroxyl radicals predominantly by US only and not due to the photo or combined sono–photo effect. Since US-promoted OH radical generation is relatively less, the rate of degradation under sonophotocatalytic conditions at higher catalyst loadings will slow down, level-off or even decrease slightly. This is consistent with the findings of Davydov *et al.*[28], who also reported that once the optimum catalyst loading is reached in sonophotocatalytic systems, higher US power has to be used to achieve further enhancement in activity.

Contrary to the progressive decrease in the concentration of phenol due to degradation, the concentration of H_2O_2 stabilizes or fluctuates due to concurrent formation and decomposition in an irreproducible manner. Hence the optimum catalyst loading for phenol degradation need not necessarily hold good for optimum H_2O_2 at any point of time.

One possibility for the formation of H_2O_2 can be the combination of hydroxyl radicals formed from water during the sono-, photo- or sonophotocatalysis. However, in the absence of any organic substrate (phenol in the current case), the quantity of H_2O_2 formed is quite low compared to that in the presence of phenol. Degradation of phenol leads to increased amounts of H_2O_2 in sono-, photo- and sonophotocatalytic systems as seen in Figure 4. This is consistent with the earlier report[25] according to which 'in-between' introduction of extra phenol to a ZnO–phenol–H_2O system under sono-, photo- or sonophoto irradiation enhances the formation of H_2O_2. This further reconfirms the role of substrate in the generation of H_2O_2. Hence it is reasonable to assume that a major part of H_2O_2 present in the system is formed concurrently with the degradation of the pollutant though the contribution of OH radicals formed from water cannot be ruled out.

The sono-, photo- and sonophotocatalytic degradation of phenol follow variable kinetics depending on the concentration of the substrate[4]. However, the effect of concentration of phenol on the oscillation does not show any consistent trend and the precise time of reaction or concentration of H_2O_2 for the occurrence of maxima and minima is not predictable as seen from the repeated experimental results (not shown here). This may be because, with too many reactive free radicals formed in the system, the recombination as well as other competing interactions may result in multiple reactions with as many intermediates. These intermediates themselves will undergo further degradation leading to even more complex combination of free radicals and eventual mineralization. Similar inconsistency is also seen in the effect of

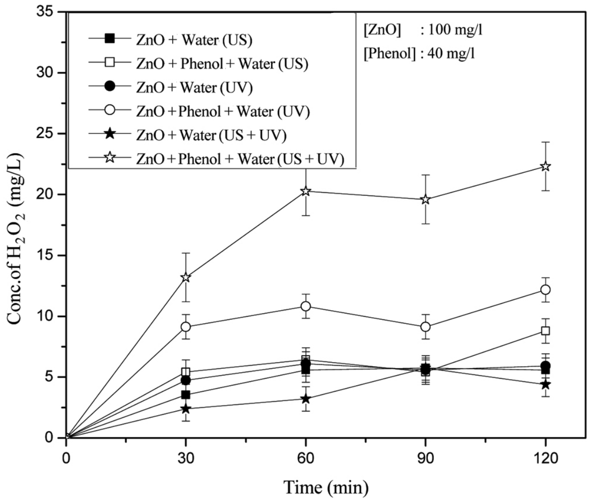

Figure 4. Influence of presence of phenol on net concentration of H_2O_2 in the sono-, photo- and sonophotocatalytic system.

pH on the phenomenon of oscillation. Repeated experiments showed that the effect of pH on the behaviour of H_2O_2 in the presence of phenol is extremely complicated possibly due to the interplay of a number of factors. The maxima and minima in the oscillation curve are present at all pH values, though the results are not consistently reproducible. H_2O_2 itself can serve as an electron acceptor or hole scavenger as follows and form free radicals required to sustain the oscillation.

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^-, \quad (6)$$

$$H_2O_2 + {}^\bullet OH/h^+ \rightarrow HO_2^\bullet + H_2O/H^+. \quad (7)$$

Serpone *et al.*[29] demonstrated that the kinetics and mechanism of photo/sono/sonophotocatalytic degradation of phenol is different at different pH values with different types of intermediates which themselves undergo different kinds of reactions. This also adds to the difficulty in delineating the effect of pH on the concentration of H_2O_2.

The current study shows that H_2O_2 decomposition is negligible in the dark or by photolysis or sonolysis in the absence of a catalyst. The formation or decomposition of H_2O_2 does not happen in the presence of alumina particles, comparable in size and surface area to ZnO. Naturally, no oscillation is observed in this case. Hence the concurrent formation and decomposition of H_2O_2 is essentially a catalytically active surface-initiated process, though it may be propagated in the homogeneous bulk as well. This is in line with the findings of Ilisz *et al.*[30].

The effect of externally added H_2O_2 on the degradation of phenol as well as its own fate under sono-, photo- and/or sonophotocatalytic conditions was experimentally verified. As expected, the enhanced number of free radicals generated from the decomposition of added H_2O_2 results in enhanced phenol degradation (Figure 5). However, corresponding increase is not detected in the case of H_2O_2 (Figure 6). In the case of photo- and sonophotocatalytic systems in which H_2O_2 is added externally, the net concentration (of H_2O_2) is not much different from the corresponding systems without any added H_2O_2 in the later stages of irradiation. In the case of the relatively slower sonocatalytic degradation of phenol, the formation as well as decomposition of H_2O_2 are also slower resulting in the net concentration of H_2O_2 (including the externally added quantity) remaining practically unchanged. This reiterates earlier inference that in sono-, photo- and sonophotocatalytic systems both the formation and decomposition of H_2O_2 compete with each other. The process is primarily concentration-dependent. At higher concentration of H_2O_2 (as in the case of external addition), the decomposition is dominant in the beginning in the case of sono- and photocatalysis and matches with the formation. This may be the reason for initial drop/stabilization in the net H_2O_2 concentration in sono- and photocatalysis. However, in sonophotocatalysis, the rates of degradation of phenol and the corresponding formation of H_2O_2 are much higher compared to sono- or photocatalysis. Hence the initial decrease in the concentration of added H_2O_2 is more than compensated by the higher formation rate. Consequently, the concentration of H_2O_2 increases fairly steeply in the beginning and slowly thereafter. Hence in the case of externally added H_2O_2, once the more dominant decomposition has brought its concentration down to moderate level, the system behaves similar to those cases in which there is no externally added H_2O_2.

In semiconductor-mediated sono-, photo- and sonophotocatalysis, the primary step involves the promotion of electron from the valence band to the conduction band (e_{cb}^-), leaving a positively charged hole in the valence band (h_{vb}^+). The electrons are then free to migrate within the conduction band. The holes may be neutralized by migration of electrons from an adjacent molecule. In the

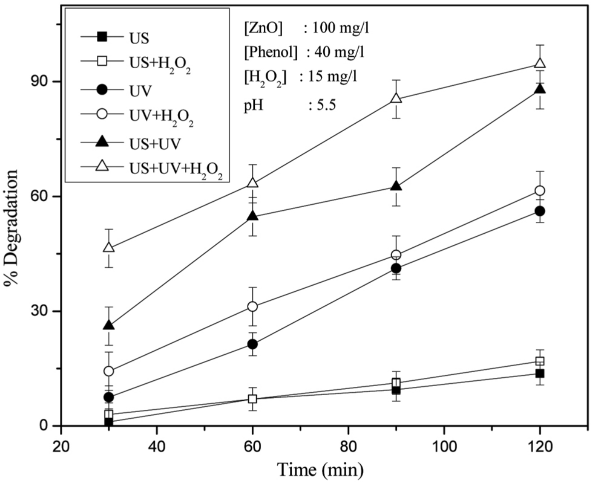

Figure 5. Effect of added H_2O_2 on the degradation of phenol under sono-, photo- and sonophotocatalysis.

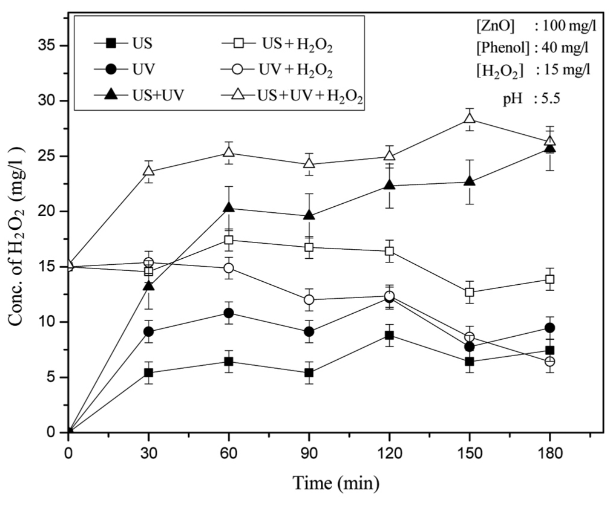

Figure 6. Effect of added H_2O_2 on net concentration of H_2O_2 under sono-, photo- and sonophotocatalysis.

process, the molecule (in the current case, phenol) gets oxidized and the process can be repeated[8]. The electrons and holes can recombine with no productive result and the efficiency of the system depends on its ability to retard the recombination. Various reactions leading to the formation of ROS such as $O_2^{-\bullet}$, $^\bullet OH$ and $HO_2^\bullet$ at the surface and their interactions have been illustrated in a number of reviews[1,8]. The free radicals $^\bullet OH$ and $HO_2^\bullet$ can give rise to H_2O_2 as in reactions (4) and (5). Further, they can interact with phenol resulting in its degradation and eventual mineralization as in reaction (3). Since the amount of H_2O_2 generated in the absence of phenol is insignificant, it is reasonable to assume that the degradation of phenol and the formation of H_2O_2 are at least partially related.

H_2O_2 is a by-product/intermediate in the degradation of phenol under sono-, photo- and sonophotocatalysis and hence its concentration is expected to increase and ultimately stabilize when the phenol degradation is complete. The oscillation/stabilization in the concentration shows that H_2O_2 is generated and decomposed/consumed simultaneously depending on the reaction conditions. When the concentration reaches a particular maximum, the decomposition dominates bringing its net concentration down. Similarly, when the concentration reaches a critical minimum, the formation process gets precedence. This process happens many times over. The degradation of phenol continues unabated even when the concurrently formed H_2O_2 shows stabilization/oscillation. The decomposition of H_2O_2 is known to take place as follows[8,24]

$$\mathrm{ZnO} \xrightarrow{\mathrm{UV/US/(US+UV)}} e_{cb} + h_{vb}, \tag{8}$$

$$H_2O_2 + \mathrm{UV/US/(US + UV)} \rightarrow 2\ ^\bullet OH, \tag{9}$$

$$2\ h_{vb}^+ + H_2O_2 \rightarrow O_2 + 2\ H^+, \tag{10}$$

$$2\ e_{cb}^- + 2\ H^+ + H_2O_2 \rightarrow 2\ H_2O, \tag{11}$$

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2^\bullet, \tag{12}$$

$$H_2O_2 + HO_2^\bullet \rightarrow H_2O + {}^\bullet OH + O_2, \tag{13}$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow {}^\bullet OH + OH^- + O_2. \tag{14}$$

Thus, the same free radicals can contribute to the formation and decomposition of H_2O_2 depending on the conditions. At the same time, being a complex free radical system, many other reactive species also may be possible, especially in sonophotocatalysis, resulting in more interactions leading to the formation and decomposition of H_2O_2.

Sono-, photo- and sonophotocatalytic degradation of phenol in water in presence of ZnO generates H_2O_2 as an intermediate as well as final product. The H_2O_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. The oscillation is concentration-dependent, with formation or decomposition dominating at any point in time leading to increase or decrease in its concentration. H_2O_2 itself can function as an electron acceptor and hole scavenger, and thus play a significant role in the oscillation as well as in the overall phenol degradation process.

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Tafoni along the east coast, Chennai to Mamallapuram, Tamil Nadu

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A study on weathering pits called tafoni was carried out on rock surfaces that age from a few hundreds to millions of years along the east coast between Chennai and Mamallapuram. Tafoni of varying sizes and shapes such as simple circular dots to oblate to prolate, hemispherical to spherical are formed on the granite, granite gneiss, charnockites (acid and mafic) and sandstone both on exposed and inner wall surfaces. In this study, their formation is related to not only tropical weathering processes, but also to sea salt water splays causing salt mineral etching, weathering processes, besides microbial activity, algal and lichen growth accentuating their formation.

Keywords: Bedrock surface, mafic minerals, tafoni, weathering processes.

WEATHERING starts generally on the rock surfaces or from their inner walls by the formation of pits[1–3]. Tafoni are pits, ellipsoidal, flat pan-like to bowl-shaped, occurring as natural rock cavities[3–9]. These cavernous weathering features include tiny pits, chemically dissolved pits, softball-sized cavities, caves and cellular honeycomb forms often lined by thin layers of dark black algae or microbial mat. Typically tafoni develop on inclined or vertical surfaces and occur in groups or clusters, and in all types of bedrocks. These cavernous weathering landforms are present on the surfaces of many different kinds of rocks located in a multitude of geographic regions around the world[1,9]. However, tafoni development and evolution are puzzling and continue to arouse curiosity[5,8–11]. Very little work has been carried out on tafoni and weathering along the east coast of Tamil Nadu from Chennai to Mamallapuram[6]. In the present communication, we describe tafoni as an important weathering type along the east coast extending from Chennai to Mamallapuram. The purpose of the study was to examine the various types and sizes of tafoni weathering features on rock surfaces of different ages, on similar/different rock types, from coastal and inland sites. Tafoni were observed over rock surfaces of different ages from a few hundred to several million years old, including on colonial grave tombstones, temple walls, sculptures (of historical periods), menhirs (ancient monumental standing stones), exposed rock outcrops, etc. Hence this study is aimed to understand the plausible causes for tafoni formation along the east coast between Chennai and Mamallapuram.

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