Sunlight activated ZnO mediated photocatalytic degradation of acetophenone in water

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Abstract: *Solar photocatalysis is investigated as a potential advanced oxidation process for the removal of small amounts of acetophenone (ACP), a recalcitrant chemical pollutant detected in the effluent water from many petrochemical and other industries. Semiconductor oxide ZnO is used as the catalyst. The influence of various reaction parameters such as initial concentration of ACP, ZnO dosage, pH of the medium, humic acid, H_2O_2, O_2, anions/salts etc on the rate of degradation is evaluated. 1- hydroxy acetophenone (HACP) is identified as the major intermediate in the degradation. H_2O_2 formed insitu in the process acts as a reservoir of various reactive oxygen species (ROS) which can enhance the degradation. However, H_2O_2 also acts as a scavenger for the ROS leading to its own concurrent decomposition. Consequently, the enhancing effect of externally added H_2O_2 is not quite significant. The degradation is slow in deaerated system thereby reconfirming the role of O_2 in the photocatalytic process. The catalyst can be recycled at least four times repeatedly before there is reduction in activity. Anions/salts inhibit the degradation mostly, though there is no consistency in their behaviour which depends on the concentration as well as reaction time. The study clearly shows that sunlight induced zinc oxide mediated photocatalysis can be used as a powerful tool for the degradation/mineralization of traces of ACP in contaminated water. Solar photocatalysis thus offers the potential for achieving the twin objectives of sunlight harvesting and wastewater treatment.*
Key words*: Zinc oxide, Photocatalysis, acetophenone, Hydrogen peroxide, Solar energy*

I.   Introduction

Heterogeneous photocatalysis, mediated by semiconductor oxides has been widely investigated as a viable Advanced Oxidation Process (AOP) for the removal trace organic pollutants such as pesticides, petrochemicals, pharmaceuticals, dyes, paper industry wastes and inorganics from water [1-7]. The added attraction of photocatalysis is the potential to use sunlight as the source of energy. Identification of suitable solar active catalysts capable of mineralizing hazardous and toxic organic pollutants into harmless end products such as CO_2, water and salts under ambient condition is an important objective of most of the investigations in this area. In this context, the potential of using simple semiconductor oxides such as ZnO or TiO_2 to harness solar energy will be a major step towards economical large-scale application of photocatalysis in water treatment. TiO_2, though more stable and abundant, absorbs mostly the UV region of solar spectrum, making it a poor candidate for direct sunlight application. Modification of TiO_2 by coupling with other semiconductors and metalizing with noble metals have been attempted to extend the absorption to the visible region of solar spectrum. However, such modifications are generally more expensive and technology intensive. Another potential candidate is ZnO which has absorption over a wider wavelength range [8-11] though it suffers from the disadvantage of instability under extreme acidic condition. Another disadvantage is the incongruous dissolution to yield $Zn(OH)_2$ on ZnO particles leading to catalyst inactivation over time. However, this problem of corrosion/dissolution can be overcome to a great extent by suitably modifying the reaction conditions, in particular the pH of the medium and optimum reaction parameters, so as to take advantage of the wider solar absorption spectrum of ZnO [12,13].

When a semiconductor is irradiated with photons of energy equal or greater than its band gap energy (~ 3.2 eV in the case of TiO_2 as well as ZnO) the photons are absorbed and electron-hole pairs are created. These electrons and holes can either recombine or migrate towards the surface participating in several redox reactions eventually leading to the formation of Reactive Oxygen Species (ROS) such as OH radicals and H_2O_2 [1,6]. The holes will react with water molecules or hydroxide ions (OH⁻) in aqueous solution to produce hydroxyl radicals, capable of oxidising many organic pollutants. These ROS can initiate and promote a number of reactions which end up in complete mineralisation of the pollutants into harmless end products.

Acetophenone (ACP) (other names: Methyl phenyl ketone, Acety benzene, CAS number: 98-86-2) is a by-product in many petrochemical industries, especially in the phenol-acetone synthesis by the cumene oxidation process. It is often found as a trace pollutant in the effluent water from such industries. ACP is a colourless to yellow-tinted liquid with a sweet strong odour and is only sparingly soluble in water. It causes

severe eyes, nose, throat and skin irritation even on short-term exposure while chronic exposure may lead to serious health effects including metabolic disorders. It is also toxic to algae and certain type of aquatic organisms. Removal of last traces of ACP from effluent water by conventional techniques is often difficult and expensive. Since ZnO photocatalysis using sunlight as the activation source has been proven to be an effective AOP for the removal of the last traces of many toxic organic pollutants such as alfa-methyl styrene and diquat from water [1-6, 13,14], the same is investigated here as a possible option for the decontamination of water containing traces of ACP.

The chemical structure of ACP (C_8H_8O, molecular weight: 120) is given in figure 1.
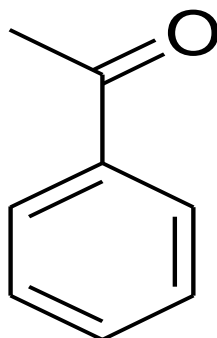
Figure 1. Chemical structure of ACP

Very few studies are reported in literature on the photo/photocatalytic degradation of ACP. These are based on expensive and 'difficult to make' metal impregnated TiO_2 catalysts [15]. The photo adsorption of ACP on TiO_2 is poor and depends on the light intensity. Other studies refer to the photo-hydrogenation of ACP. However no detailed studies on the photocatalytic degradation/mineralization of trace amounts of ACP in water seem to be reported so far. In the current paper we are reporting the results of our investigations on photocatalytic mineralisation of trace amounts of ACP in water using sunlight as the energy source and commercially available ZnO as catalysts. The results clearly show that heterogeneous photocatalysis is a viable tool for the complete removal of ACP from water.

II. Materials and Methods

ACP (99.9%) was obtained from Merck India and used as such without further purification. Zinc oxide (>99% purity) with BET surface area ~10 m^2/g was obtained from Merck Chemical Company (India). LR grade H_2O_2 and HCl were from Nice chemicals India. The reaction solutions/reagents were prepared in Millipore water. The ZnO was characterised by SEM and XRD measurements. Pore size analysis was made using Micrometrics Tristar surface area and porosity analyser. The average pore width is 123 Å. Approximate size distribution is; < 250Å (70.1%), 250-500 Å (11.3%) and > 500 Å (17.8%). The average particle size is 3.2 μm, as analysed using Malvern Mastersizer 3000.
Adsorption studies were performed as follows:

A fixed amount (0.1 g) ZnO was suspended in 100 ml of ACP solution in a 250 ml reaction flask. The pH was adjusted as required. The suspension was agitated continuously at constant temperature of 29 ± 1^{0}C for 2 hrs to achieve equilibrium. It was then kept undisturbed for 2 hr. followed by centrifugation at 3000 rpm for 10 min. After centrifugation the concentration of ACP in the supernatant was determined by gas chromatography (GC). Keeping the suspension overnight before centrifuging did not make any significant difference in the concentration of ACP in the supernatant indicating that the 2 hr period is adequate to complete the adsorption.

The adsorption was calculated from the relation
$$q_e = (C_0 - C_e)V/W \qquad (1)$$
where C_0 is the initial adsorbate concentration (mg/L), C_e is the equilibrium adsorbate concentration in solution (mg/L), V is the volume of the solution in Litre, W is the mass of the adsorbent in gram and q_e is the amount adsorbed in mg per gram of the adsorbent.

Photocatalytic experiments in presence of sunlight were performed in a jacketed pyrex reactor. The ACP solution (60 ml) together with ZnO was taken in the inner compartment and cooling water from a thermostat (29± 1^0C) was circulated through the outer jacket. Solar experiments were performed by placing the system on the roof top of our laboratory at Kochi, Kerala, India (9^0 57' 51" N, 76^0 16' 59" E) during sunny days in April-May, September-October 2013, February-May, September-October 2014 and March - May 2015. The suspension was stirred frequently to ensure uniform mixing. The average intensity of solar light during the experiments was 1.25×10^5 Lux, as calculated from the measurements using LT-Lutron LX-101A Digital Lux meter. A reference experiment using the same type of reactor and identical reaction parameters was conducted with every set of experiments to ensure the consistency and reliability of the results. Samples from the photocatalytic reactor were drawn periodically, filtered through 0.45µm filter and analyzed for the ACP remaining as well as for other intermediates/products by Gas Chromatography using flame ionization detector and Elite 1301 column with hydrogen carrier gas. The instrument was earlier calibrated for quantitative estimation of the ACP at comparable concentrations. Suspension kept under identical conditions in the dark was used as the reference in each case to eliminate the contribution from adsorption and dark reaction, if any, towards the reduction in the pollutant concentration.

The formation of hydroxyl radicals on the surface of ZnO during solar irradiation is tested by the photoluminescence (PL) technique using terephthalic acid (TPA) as the probe molecule [16]. The hydroxyl radicals formed *in-situ* in the system reacts with TPA and form 2- hydroxyl terephthalic acid (HTPA). The fluorescence intensity of HTPA formed is proportional to the formation of ˙OH radicals in the system. In this method, ZnO (0.03 g) is suspended in a mixed aqueous solution of TPA (2×10^{-4}M) and NaOH (2×10^{-3}M) and irradiated by sunlight. The PL spectrum of the product HTPA is recorded in the range of 400 -450 nm after every 5 minutes of irradiation. The excitation wavelength was 315 nm. The PL intensity at 425 nm corresponds to the concentration of HTPA. Shimadzu model RF-5301PC fluorescence spectrophotometer is used for recording the spectrum.

III. Results and Discussion

Commercially available ZnO sample was compared with those prepared in the laboratory from three different precursors, i.e. $ZnCO_3$, $Zn(NO_3)_2$ and $Zn(OH)_2$ by standard procedures. Physico-chemical characterization such as adsorption, BET surface area, XRD and SEM showed that they are identical to commercial ZnO. Typical XRD and SEM image of ZnO used in the study are shown in figures 2A and B.
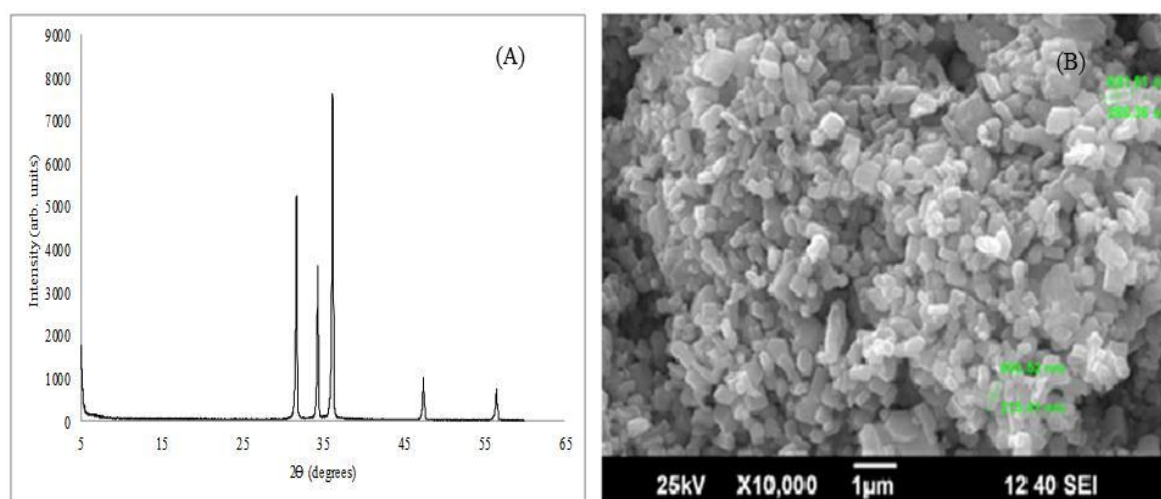

Figure 2: (A) XRD of ZnO (B) SEM image of ZnO.

Preliminary studies showed that the photocatalytic activity of all the prepared catalysts was also comparable with that of commercial ZnO. Since the home-prepared catalyst did not have any specific advantage in terms of catalytic activity or stability, all further studies reported here were carried out using the readily available, relatively less expensive commercial ZnO.

Studies on the photocatalytic degradation of ACP (30 mg/L) in presence of sunlight, using ZnO (0.10 g/L) as the catalyst, showed facile steadily increasing degradation with time. HACP is identified as the major intermediate. Typical chromatogram showing the formation of small but significant quantities of HACP is shown in figure 3. The small peak at 20 minutes corresponds to HACP. The concentration of HACP increases initially with decrease in the concentration of ACP to level off (figure 4).
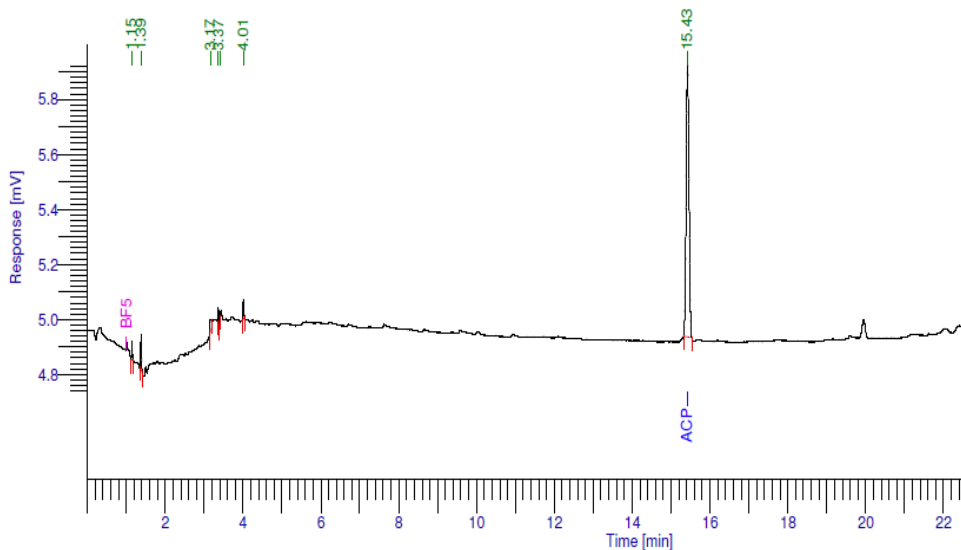
Figure.3. Typical chromatogram showing ACP and HACP
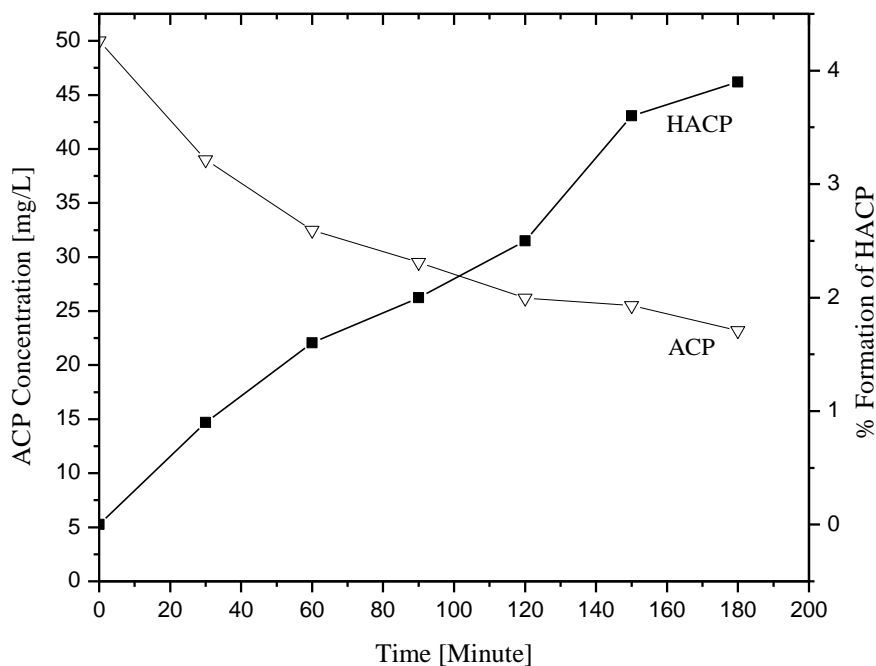
Figure 4. Photocatalytic degradation of ACP and concurrent formation of HACP

Continued irradiation results in the disappearance of HACP also thereby demonstrating the capability of the process for complete mineralization. The degradation is close to 100% in 60 minutes when the concentration of ACP was 5 mg/L. No degradation was observed in parallel experiments under identical conditions in the absence of light or catalyst. The adsorption of ACP on ZnO under the experimental conditions is low ($< \sim 5\%$) at all concentrations studied here, thereby showing that the decrease in concentration is due to degradation and/or mineralization. Generally, adsorption of substrate on the catalyst surface is considered as a prerequisite for effective photocatalytic degradation. However, the interactions with the reactive species and/or surface-generated reactive free radicals can take place in the bulk as well as is evident from the high degradation rate of ACP, in spite of its poor adsorption. This is in line with the observations by Turchi and Ollis [17] who demonstrated that though photocatalytic degradation depends on the adsorptive properties of the organic compounds on the surface, it is not an essential requirement for the reactions. The reactive OH radicals and other oxidizing species can diffuse into the bulk solution to interact with the organic pollutant.

Since adsorption of the substrate is not a major factor, the decrease in degradation rate with time is possibly due to decrease in the concentration of ACP and the competition between the reaction intermediates and ACP for the reactive free radicals. Other than HACP, only one minor (practically insignificant) intermediate is detected during the reaction which is tentatively identified as phenol. Eventually the intermediates also gets degraded and mineralised as seen from their complete disappearance with time. The chemical oxygen demand (COD) of the reaction solution also decreases` steadily and reaches '0', thus confirming complete mineralization. See Figure 5.

3.1. Effect of catalyst dosage

The effect of catalyst loading on the degradation of ACP is investigated by varying the amount of zinc oxide from 0.02 to 0.18 gL^{-1}, keeping all other parameters identical. The degradation increases with increase in catalyst loading upto 0.10 g/L and stabilises/ decreases slightly thereafter. The enhanced degradation at higher catalyst loadings is usually attributed to the increased number of adsorption and interaction sites for the substrates and/or the intermediates and more effective absorption of light. However, in the current instance, the adsorption of ACP on ZnO is not significant and hence the role of the catalyst is maximising the light absorption and consequent formation of higher number of reactive hydroxyl and other radicals. These reactive species result in increased interactions with the pollutant. Any further increase in catalyst concentration beyond the optimum will only result in scattering and reduced passage of light through the suspension medium. Another reason may be the aggregation of catalyst particles causing decrease in the number of available active surface sites. The particles cannot be
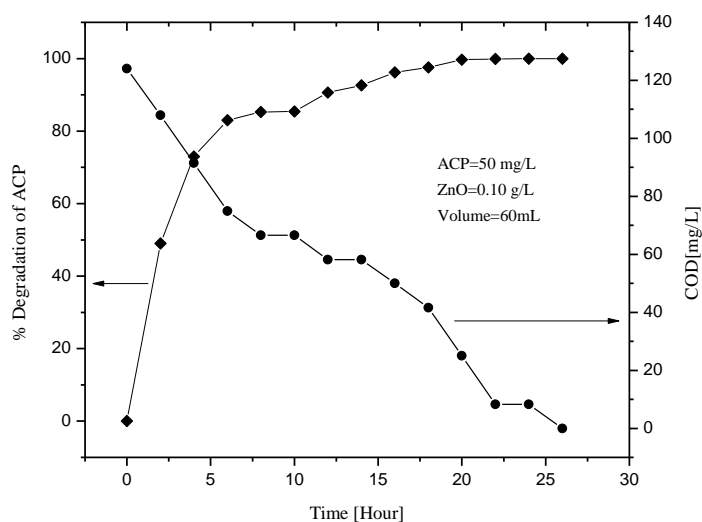
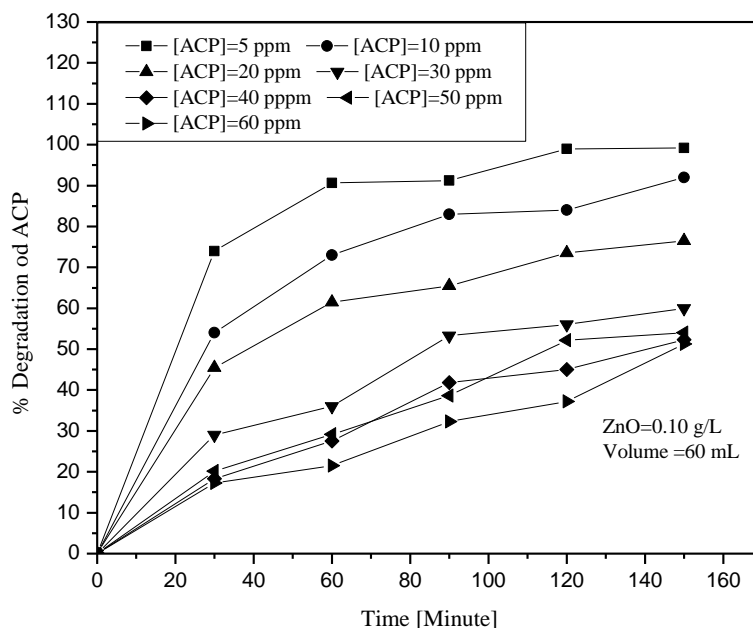**Figure. 5**. Photocatalytic degradation of ACP and concurrent variation in COD

fully and effectively suspended beyond a particular loading in a particular reactor which also leads to suboptimal penetration of light and reduced adsorption of the substrate on the surface. It is also possible that at higher loading, part of the activated zinc oxide (ZnO*) gets deactivated (ZnO[#]) through collision with ground state catalyst according to the following equation [18]:

$$ZnO* + ZnO \longrightarrow ZnO^{\#} + ZnO \quad (2)$$
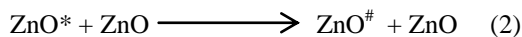
However, the optimum catalyst loading is applicable only for the specific reaction conditions and will depend on a number of factors including the size, shape and geometry of the reaction assembly. Hence, the optimization has to be made separately for each reactor configuration. In the present case the optimum loading of ZnO is 0.10 g/L. Hence all further studies were carried out with this loading.

3.2. Effect of initial concentration of ACP

The effect of initial concentration of ACP in water on its solar photocatalytic degradation is investigated in the range of 5-60 mg/L. (Figure 6A). It is observed that the percentage degradation decreases as the concentration of ACP increases.   In contrast, the rate of removal increases steadily with increase in the initial concentration of ACP and stabilizes/decreases eventually (Figure 6 B). As is evident from the

Figure 6A. Effect of concentration of ACP on its photocatalytic degradation
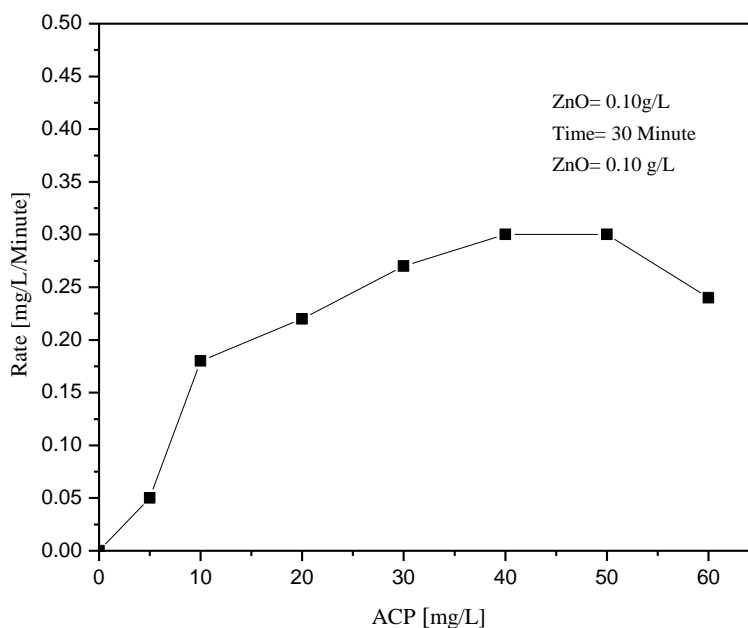
Figure.6B.Effect of concentration of ACP on its photocatalytic degradation rate

graph, the rate follows variable kinetics at various concentrations of ACP. The optimum kinetic rate of 3.0 x10^{-1} mg/L/min is reached at 40 mg/L of ACP. This is followed by almost constant degradation rate at higher concentration implying zero order kinetics.

The photocatalytic degradation of many pollutants is reported to follow pseudo first order kinetics [19-21]. The increase in degradation with increase in concentration is explained as due to increase in adsorption of the substrate on the catalyst which will continue until the surface is fully covered and all the active sites are occupied. However, this is not applicable in the current instance since the adsorption of ACP on ZnO is quite low. At the same time, as the concentration increases, there will be more ACP molecules available in the bulk as well as in the proximity of the surface which can interact with the surface-generated active free radicals and ROS such as ·OH and H_2O_2. At higher concentration beyond the optimum as above, at least a part of the incident sunlight may be blocked and/or absorbed by ACP and the intermediates thereby reducing the photons available for catalyst activation. Another reason may be that major portion of the reaction occurs in the region (reaction zone) close to the irradiated side where the irradiation intensity is much higher than the other side. This retardation in the penetration of light, at longer distance from the light source, results in decreased degradation [22-25]. As the initial concentration of ACP increases, the requirement of catalyst surface needed for maintaining corresponding rate of degradation also increases. Since illumination intensity and catalyst concentration are maintained constant, the relative number of ROS generated for interacting with the ACP also presumably decreased leading to stabilized/ decreased rate of degradation.

Once the concentration of the substrate is enough to interact with all the optimum available ROS and other reactive free radicals, any further increase cannot result in increased reaction. Hence the ACP removal becomes independent of its concentration. It is also possible that at higher substrate concentration, some of the reaction intermediates may get adsorbed onto the surface or remain in the bulk for relatively longer period resulting in less frequent interaction between fresh ACP molecules and the ROS. Complete domination of the reaction system by the reactant/ intermediates can also result in suppression of the generation of surface initiated reactive free radicals. However, at any point in time, there will be an optimum for the number of substrate molecules that can interact with the reactive free radicals generated by the surface. This optimum will depend on a number of parameters such as initial

concentration of the substrate, intensity of illumination, wavelength of light, mass and type of photocatalyst, type and geometry of photoreactor etc. Consequently the measurements and calculations apply only to the specific reaction conditions and cannot be generalized.

3.3. Effect of pH

The surface characteristics of the catalyst as well as the chemical nature of the substrate and species derived from them change with the pH. Hence the pH of the reaction medium can have significant effect on the aqueous phase photocatalytic process. The point of zero charge (PZC) of ZnO is ~ 9.3. At pH values < 9.3, the catalyst's surface is positively charged and at pH values > 9.3 it is negatively charged. Depending on the ionic form of the organic compound, i.e. anionic, neutral or cationic, electrostatic attraction or repulsion takes place and the photodegradation rate can be enhanced or inhibited.

The effect of pH on the photocatalytic degradation of ACP is tested by varying the pH of the medium from 2 to 12 keeping other parameters constant. The results are presented in Figure 7. It is observed that

ACP =50 mg/L
ZnO = 0.10 g/L
Time = 30 Minute
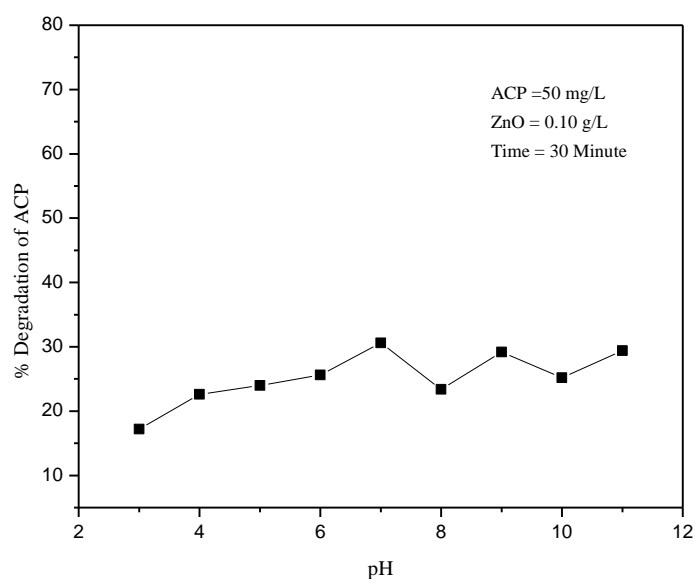
Figure 7. Effect of pH on the photocatalytic degradation of ACP

the degradation is not influenced by pH significantly in the range 4-11 even though slight increasing trend is seen towards the alkaline pH. This is expected since the adsorption of ACP on ZnO is observed to be very low and hence pH, which affects the surface of the catalyst primarily cannot influence any surface initiated process such as generation of reactive free radicals and other ROS. The very low degradation at pH=2 may be due to the corrosion of ZnO at lower pH and consequent decrease in the availability of enough active surface sites. Poulios et al. [26] also reported similar observations.

The influence of pH on the photocatalytic activity of ZnO is often inconsistent and hence cannot be generalized. A complex interplay of many factors, i.e. chemistry of the surface, extent and mode of adsorption (of ACP, HACP and/or other minor unidentified intermediates in this case), concentration of reactive free radicals such as ˙OH etc determines the pH effect in many cases. Since the adsorption of the substrate is poor in the present case, the pH effect mostly influences the surface-initiated generation of reactive ˙OH radicals and other ROS. Since the photocatalytic generation of reactive species is facilitated by both electrons and holes, the net effect at any particular pH may be more or less the same. This may be the reason for the absence of any significant pH effect.

3.4. Effect of added H_2O_2/Oxidants

H_2O_2 is an effective oxidant which enhances the photocatalytic degradation of many pollutants by providing additional reactive ˙OH radicals. H_2O_2 is also formed as a by-product during the degradation of many
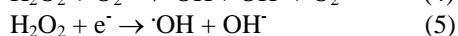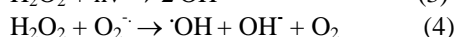
organics by AOPs. The effect of externally added H_2O_2 at different concentrations on the degradation of ACP is investigated and the results are shown in Fig.8.

Added H_2O_2 enhances the degradation of ACP moderately at all concentrations. The extent of enhancement stabilizes at higher concentration (>10 mg/L) of H_2O_2, especially in the early stages of reaction. However, at lower concentrations (<10 mg/L) of H_2O_2, initially there is enhancement followed by 'no effect' later on. This concentration-dependent inconsistency may be because of the dual role of H_2O_2 as promoter as well as inhibitor in photocatalytic systems. Further, the H_2O_2 formed insitu undergoes concurrent formation and decomposition resulting in oscillation in its concentration. Hence the net concentration of H_2O_2 in the system is not consistent or predictable at any point in time. The oscillation in the concentration as well as the role of H_2O_2 as promoter or inhibitor is concentration-dependent while the concentration itself is dependent on the competing reactions taking place in the system [20].
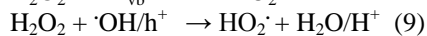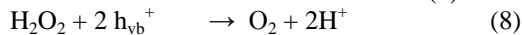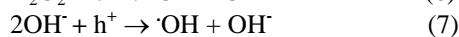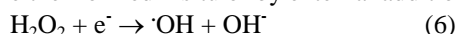
The dual role of H_2O_2 as a promoter as well as inhibitor of photocatalytic degradation has been reported by others also [13,25,27]. Other factors important in this respect are the concentration of reactants, reaction conditions and the nature of interactions. The enhancement by H_2O_2 is explained based on its role as an electron acceptor and consequent inhibition of the recombination of photogenerated electrons and holes. H_2O_2 can also produce reactive ·OH radicals as follows:
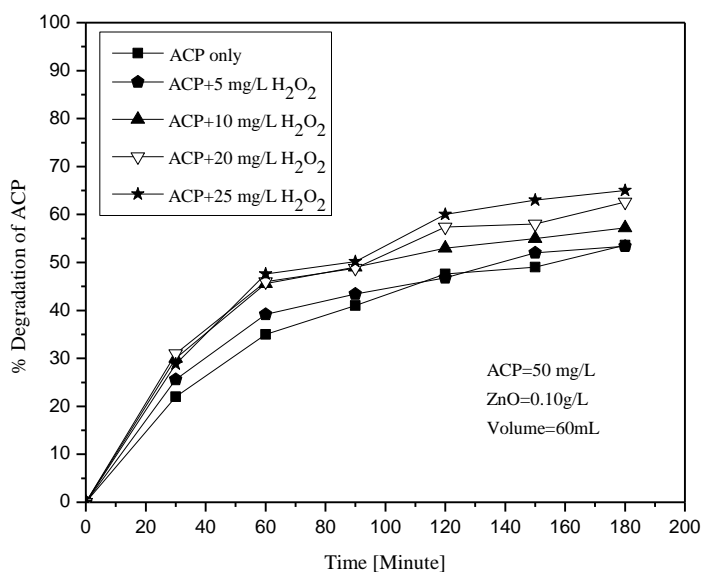
Figure 8. Effect of added H_2O_2 on the photocatalytic degradation of ACP

$$H_2O_2 + h\nu \rightarrow 2·OH \qquad (3)$$
$$H_2O_2 + O_2^{·-} \rightarrow ·OH + OH^- + O_2 \qquad (4)$$
$$H_2O_2 + e^- \rightarrow ·OH + OH^- \qquad (5)$$

These .OH radicals can enhance the degradation of the pollutant. However, at higher concentrations of H_2O_2, either formed insitu or by external addition, it acts more as scavenger of ·OH as well as holes as follows:

$$H_2O_2 + e^- \rightarrow ·OH + OH^- \qquad (6)$$
$$2OH^- + h^+ \rightarrow ·OH + OH^- \qquad (7)$$
$$H_2O_2 + 2 h_{vb}^+ \rightarrow O_2 + 2H^+ \qquad (8)$$
$$H_2O_2 + ·OH/h^+ \rightarrow HO_2· + H_2O/H^+ \qquad (9)$$

Thus it becomes a major competitor to the substrate for the ROS both on the surface of the catalyst as well as in the solution bulk, leading to its own self-decomposition. Earlier studies have shown that the adsorption of H_2O_2 on ZnO is negligible and hence most of it will be in solution. This also contributes to its competition with the substrate in the bulk. Hence the enhancing effect of added H_2O_2 is less prominent at higher concentration. In this context, the effect of two other powerful oxidants, i.e. IO_3^- and $S_2O_8^{-2}$ (both sodium salts) were also tested for their impact on the photocatalytic degradation of ACP. In this case also the effect is

negligible. It is also possible that the sunlight as such is not powerful enough (as UV source) to activate the oxidants and create the reactive species SO_4^{-} and IO_3^{-} for facilitating the degradation.

3.5. Effect of Humic acid

Humic substances that are naturally present in water are reported to enhance as well as inhibit the photocatalytic degradation of many water pollutants depending on the characteristics of the substrate, catalyst as well as the reaction conditions [28,29]. The effect of humic acid (HA) on the ZnO mediated photodegradation of ACP is investigated and the preliminary results are plotted in Figure 9. HA clearly inhibits the degradation. The extent of inhibition is dependent on the concentration of HA, higher the concentration, greater the inhibition.
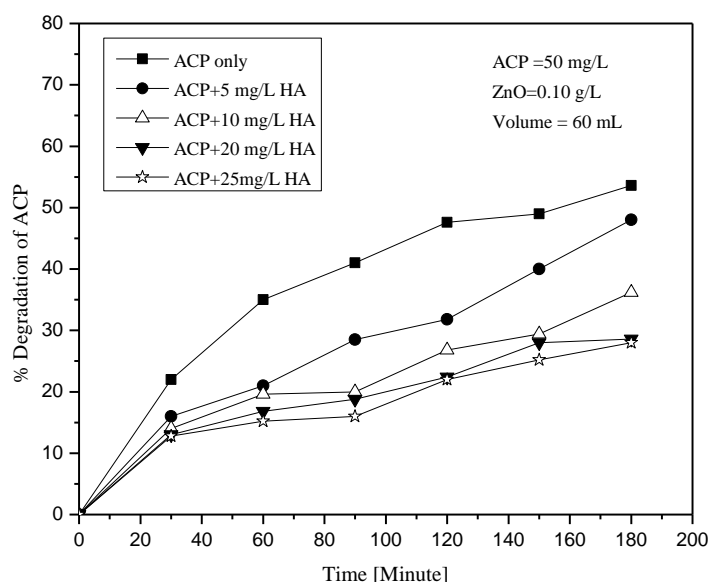
**Figure.9**.Effect of Humic acid on the photocatalytic degradation of ACP

Natural organic matter in water may absorb light thereby reducing the quantum of light available for the catalyst and thus inhibiting the photocatalytic effect. The formation of free radicals such as OH and the reactive H_2O_2 requires adequate light energy and hence the fraction of light intensity available for the surface/bulk is important. HA is also an effective free radical scavenger which can consume ROS such as $\cdot OH/ HO_2^{\cdot}/O_2^{-}$ as follows [28,29]:

$$HA + h\nu \rightarrow \qquad HA^* \qquad (10)$$
$$\cdot OH, HO_2^{\cdot}, O_2^{-} \text{ etc } + HA^* \qquad \rightarrow \text{Intermediates} \rightarrow \text{Oxidised products} \qquad (11)$$

The excited HA will decompose/get oxidised eventually. The results show that even at low concentration of HA, which is comparable to that present in natural water in local streams and ponds, HA inhibits the degradation of ACP.

3.6. Role of oxygen

Reactive oxygen species generated during the irradiation of semiconductor oxide – aqueous suspensions play important role in photocatalytic degradation of organic pollutants. Both dissolved as well as adsorbed O_2 scavenge the electrons generated on photoactivated ZnO forming superoxide radical anion and other reactive species thereby inhibiting the recombination of electrons and holes. Thus both will be available for the formation of reactive free radicals to interact with and degrade the pollutant. The role of dissolved O_2 and superoxide ion in TiO_2 photocatalysis was quantitatively demonstrated by Hirakawa et al. [30]. In order to verify the role of O_2 on the ZnO- photocatalytic degradation ACP, the reaction system is deoxygenated with N_2 and the experiments were carried out under otherwise identical conditions. The results are shown in Figure 10.
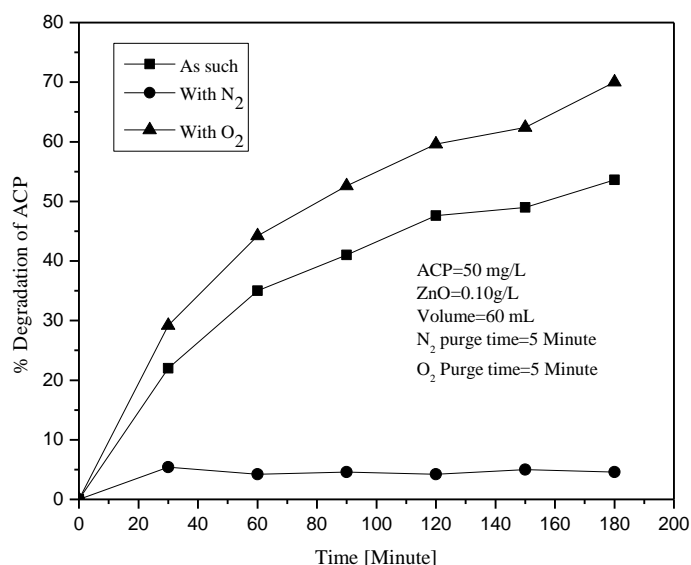
Figure 10. Effect of O_2 on the photocatalytic degradation of ACP

The photocatalytic degradation is almost fully inhibited in the absence of O_2. This essential role of O_2 is further confirmed by re-enriching the system with O_2. The degradation of ACP in this case is significantly more than that in the aerated system. The slight degradation in deaerated system may be effected possibly by the adsorbed and the dissolved O_2 which cannot be fully removed by deaeration. The available O_2 is fully consumed in the first 30 minutes itself and the degradation does not proceed further thereafter.

3.7. Effect of salts/anions

Natural water contains considerable amount of different types of dissolved salts and suspended solids which may affect the efficiency of aqueous processes. The suspended materials can be removed by physical processes. However, the dissolved salts cannot be removed that easily and it is important that any viable technology for the mineralization of pollutants in water must take the effect of these salts on the efficiency also into consideration. The inorganic ionic species present in the medium can compete with the substrate as well as the intermediates for the active surface sites. Further they can interact with the ROS and deactivate them. Other effects include; reducing the quantum of solar radiation reaching the catalyst surface, unwanted by-products etc. These processes can affect the photocatalytic degradation and mineralization efficiency [8, 26, 31,32]. The effect of the salts/anions may be further complicated by factors such as pH, nature of catalyst, substrate, concentration of the species etc. In this context, the effect of some of the commonly encountered salts in municipal and industrial wastewater on the efficiency pf ACP degradation is examined. The anions tested include; fluoride (F⁻), chloride (Cl⁻), bromide (Br⁻), iodide (I⁻), sulphate (SO_4^{2-}), nitrate (NO_3^-), phosphate (PO_4^{3-}), acetate (CH_3COO^-), oxalate ($C_2O_4^{2-}$), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). The effect of these anions was tested at different concentrations and extended duration of reaction. The reaction time as well as concentration of the anions influences the degradation differently as shown in Figures 11A and B.

At lower concentration of 5 mg/L and early reaction time of 30 min, the halides inhibit the degradation in the order I⁻ > F⁻ > Br⁻ ≈ Cl⁻. SO_4^{2-} enhances moderately. In the case of CH_3COO^-, NO_3^- and $C_2O_4^{2-}$, the effect varies from slight inhibition /'no effect'/slight enhancement. CO_3^{2-} and HCO_3^- also inhibit the degradation slightly. PO_4^{3-} inhibits the degradation strongly. The inhibition effect may be summarised as PO_4^{3-} > HCO_3^- > CO_3^{2-} ≈ I⁻ ≈ F⁻ > Cl⁻ ≈ Br⁻ ≈ CH_3COO^- > NO_3^- (no effect) > $C_2O_4^{2-}$ (slight enhancement) > SO_4^{2-} (enhancement). The inhibition/enhancement at higher reaction time may be summarised as PO_4^{3-} > CH_3COO^- > I⁻ > HCO_3^- > $C_2O_4^{2-}$ > Cl⁻ > Br⁻ > CO_3^{2-} ≈ NO_3^- (no effect) ≈ SO_4^{2-} (no effect) > F⁻ (slight enhancement). At higher concentration of anions, the effect is different. In this case F⁻ and SO_4^{2-} are strong enhancers while Cl⁻ and $C_2O_4^{2-}$ are

moderate enhancers. Other anions inhibit to varying degrees. PO_4^{3-} remains strong inhibitor throughout.
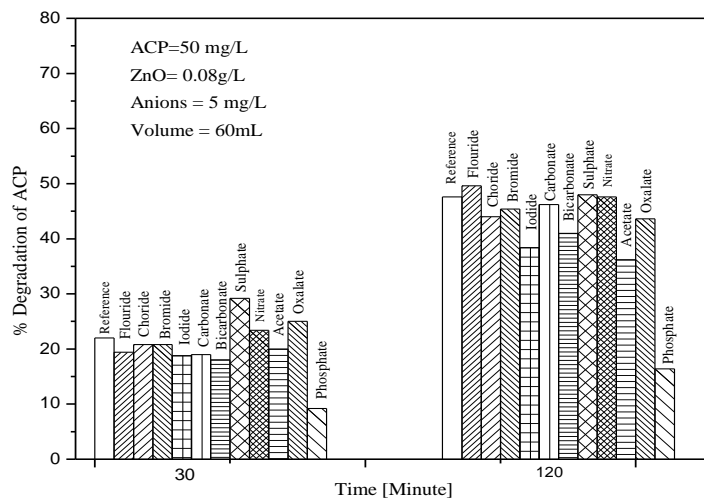

Figure.11A.Effect of anions on the degradation of ACP after different reaction times
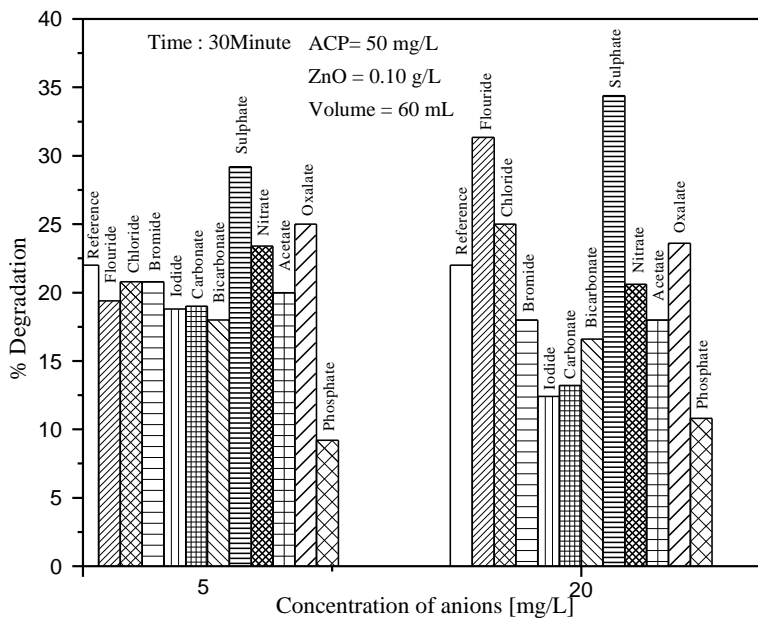

Figure.11B. Effect of various anions at different concentrations on the degradation of ACP

    Thus it is seen that no consistent pattern is emerging from the results. These anions are known to interact with the reactive ˙OH radicals and deactivate them. They also get adsorbed on the catalyst surface, thus blocking the surface sites from adsorption by the substrates and also inhibiting the formation of reactive species [11]. In the case of halides, the ions X⁻ can function as OH radical scavenger and form less active $X_2^{˙-}$ or ˙XOH⁻

radicals which can inhibit the degradation of the substrate, in this case ACP. The slight enhancement by SO_4^{2-} can be attributed to the formation of $SO_4^{\cdot-}$ radical by interaction of the anion with the photo-generated holes:

$SO_4^{2-} + h^+ \qquad \rightarrow \qquad SO_4^{\cdot-}$ (12)
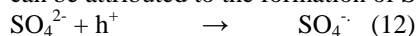
The $SO_4^{\cdot-}$ radical can accelerate the degradation process as follows:

$SO_4^{\cdot-} + H_2O \qquad \rightarrow \qquad SO_4^{2-} + \cdot OH + H^+ \qquad$ (13)

$SO_4^{\cdot-} + ACP \qquad \rightarrow \qquad$ Intermediate $1 \rightarrow \qquad$ Intermediate $2 ...... \rightarrow CO_2 + H_2O + SO_4^{2-}$ (14)
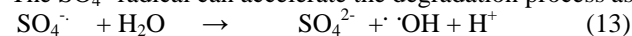
However, the simultaneously occurring inhibition by blocking other surface initiated reactions such as formation of $\cdot OH$ partially offsets the enhancement as above and the net result is moderate enhancement or inhibition or no effect depending on the domination of either of the processes or their mutual neutralization.

3.8. Recycling of the catalyst

The used ZnO is separated from the reaction system by simple centrifugation, air dried at room temperature (~30^0C) and reused to evaluate the possibility of recycling the used catalyst for the photocatalytic degradation of ACP. The photocatalytic activity is retained for multiple runs as shown in Figure.12.

The catalyst remains active at least for 4 recycles before the activity decreases. This is an important factor for scaling up the process and eventual commercialization. Based on similar observations from our laboratory on the photocatalytic degradation of alpha-methyl styrene on recycled ZnO, it may be inferred that decrease in adsorption of the substrate, in relation to fresh catalyst and formation of surface hydroxides are two major factors leading to decreased activity of continuously recycled ZnO, even though other factors also cannot be ruled out. The number of possible recycling before the decline in activity may vary depending on the reaction conditions, chemistry of the substrate and its intermediates, reactor size and geometry etc
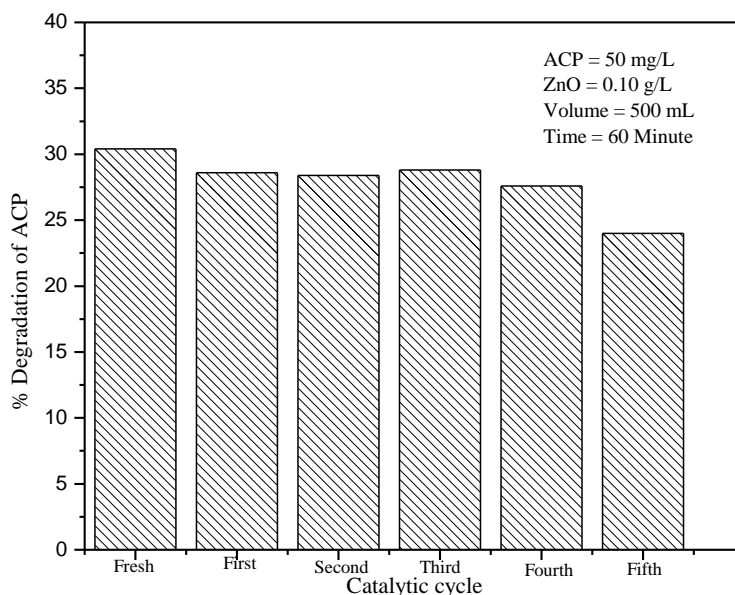
Figure 12. Recycling of ZnO for the photocatalytic degradation of ACP

IV. General mechanism

The first step in semiconductor photocatalysis is the absorption of light by the catalyst and creation of electron-hole pair:

$ZnO + h\nu \qquad \rightarrow \qquad ZnO (h^+_{vb}) + ZnO (e^-_{cb}) \qquad$ (15)
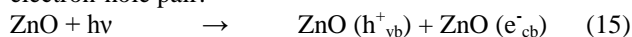
Consequently the electron is promoted from the valence band of the semiconductor to its conduction band, creating corresponding hole (+ ve charge) in the valence band. The semiconductor can function as an effective photocatalyst when both the electron and hole are consumed. It is generally accepted by researchers that both

the electrons and holes can find low energy trap sites on a sub-picosecond time scale in the semiconductor [31]. The electrons and holes can recombine and dissipate the input energy as heat and in such case photocatalysis cannot take place. Alternatively, they can react with electron donors and electron acceptors which are adsorbed on the semiconductor surface and/or trapped within the surrounding electrical double layer of the charged particles to produce strong oxidizing ˙OH radicals [32]. These radicals can promote the oxidation of organic compounds as follows:

$$O_2 + e- \rightarrow O_2^{\cdot-} \qquad (16)$$
$$h^+ + H_2O \rightarrow h^+ + \cdot OH \qquad (17)$$
$$\cdot OH + RH \rightarrow H_2O + R^{\cdot} \qquad (18)$$
$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \rightarrow Intermediate(s) \rightarrow \rightarrow CO_2 + H_2O \quad (19)$$
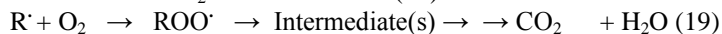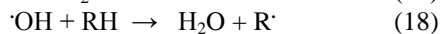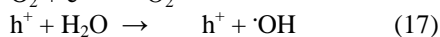
RH is ACP and the major intermediate is HACP in the current instance.
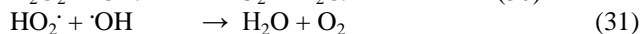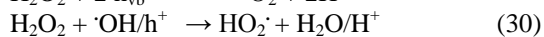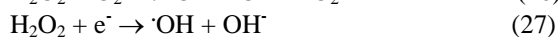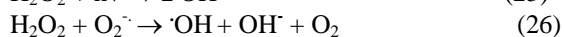
The formation of ˙OH radicals on the surface of the solar irradiated ZnO is confirmed by the photoluminescence technique as explained earlier. Solar irradiation of the ZnO-TPA system shows gradual increase in the PL intensity at 425 nm with time of irradiation, as shown in Figure 13. This is attributed to the formation of HTPA by the interaction of ˙OH radicals formed insitu on the surface of ZnO with TPA during solar irradiation of the system. No PL was observed in the absence of sunlight and ZnO thereby confirming the role of these two components on the formation of reactive ˙OH radicals. H_2O_2 is detected as a co-product as well as intermediate in the photocatalytic degradation of many organic compounds [1-3,17,20,25]. However, its concentration does not increase in proportion to the degradation of the pollutant and is stabilised or even decreased even before the pollutant degradation is complete. This has been explained as due to the oscillation in the concentration of H_2O_2 arising due to the simultaneous formation and decomposition [12,33]. The concentration of H_2O_2 increases initially, decreases then and increases again. Depending on the domination of the formation or decomposition rate, the net concentration of H_2O_2 at any point of time varies.
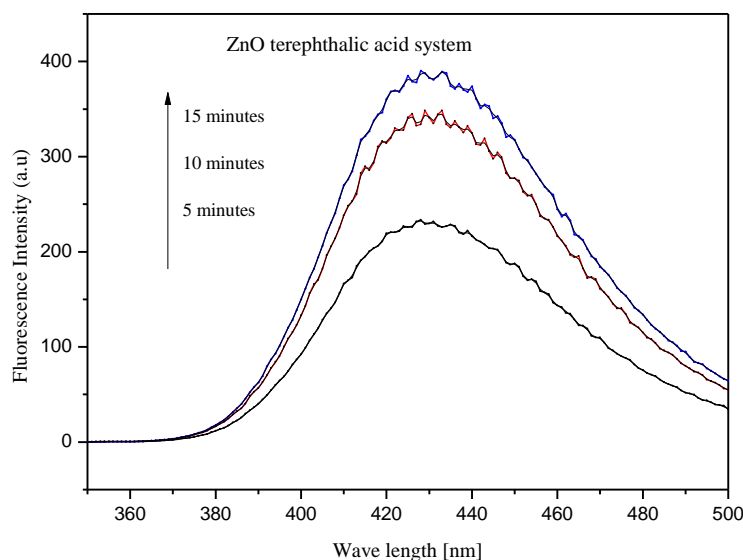
Figure 13. PL spectral changes indicating the presence of .OH radicals during ZnO photocatalysis

Various steps leading to the concurrent formation (reactions 20-24) and decomposition (reactions 25-31) of H_2O_2 may be summarized as follows [12,20,33-35]:

$$O_2^{\cdot-} + H^+ \rightarrow HO_2^{\cdot} \qquad (20)$$
$$2 HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (21)$$
$$O_2^- + HO_2^{\cdot} \rightarrow O_2 + HO_2^{\cdot-} \qquad (22)$$
$$HO_2^{\cdot-} + H^+ \rightarrow H_2O_2 \qquad (23)$$
$$\cdot OH + \cdot OH \rightarrow H_2O_2 \qquad (24)$$

$$H_2O_2 + h\nu \rightarrow 2\,^{\cdot}OH \qquad\qquad (25)$$
$$H_2O_2 + O_2^{\cdot -} \rightarrow\, ^{\cdot}OH + OH^- + O_2 \qquad\qquad (26)$$
$$H_2O_2 + e^- \rightarrow\, ^{\cdot}OH + OH^- \qquad\qquad (27)$$
$$2OH^- + h^+ \rightarrow\, ^{\cdot}OH + OH^- \qquad\qquad (28)$$
$$H_2O_2 + 2\,h_{vb}^+ \quad\rightarrow\, O_2 + 2H^+ \qquad\qquad (29)$$
$$H_2O_2 + \,^{\cdot}OH/h^+ \rightarrow HO_2^{\cdot} + H_2O/H^+ \qquad (30)$$
$$HO_2^{\cdot} + \,^{\cdot}OH \quad\rightarrow H_2O + O_2 \qquad\qquad (31)$$

Repeated attacks by the $O_2^{\cdot -}/^{\cdot}OH/HO_2^{\cdot}$ radicals on the pollutant nuclei ultimately lead to the mineralization producing mainly CO_2 and water. This is further confirmed by the progressive decrease and eventual disappearance of chemical oxygen demand (COD) as the reaction progresses, as shown earlier.

V. Conclusions

The photocatalytic degradation of trace amounts of acetophenone in water is investigated in the presence of ZnO as catalyst with sunlight as the energy source. The degradation proceeds well and 1-hydroxy-acetophenone (HACP) is identified as the major intermediate. Eventually, HACP also gets mineralised and the chemical oxygen demand becomes 'nil' indicating the potential application of solar energy for the photocatalytic removal of toxic pollutants from water. The concentration of concurrently formed H_2O_2 does not increase corresponding to the degradation of ACP and is oscillating with crests and troughs. This phenomenon is attributed to the simultaneous and competing formation and decomposition processes. The degradation of ACP is slow in deaerated system thereby confirming the essential role of O_2 in photocatalytic processes. The reaction rate depends on parameters such as pH, substrate concentration, catalyst dosage, presence of cross contaminants in water, oxidants, humus materials etc. The catalyst can be recycled at least four times with comparable efficiency. The study reiterates the possibility of using ZnO as a semiconductor oxide catalyst for the dual application of harvesting solar energy and the removal of hazardous pollutants from water.

References

[1] M. R. Hoffmann, S. T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95,1995, 69-96

[2] U. I. Gaya, A. H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems, J. Photochem. Photobiol. C: Photochem. Rev. 9, 2008, 1-12

[3] S. Devipriya, S. Yesodharan, Photocatalytic degradation of pesticide contaminants in water, Solar Energy Materials and Solar Cells, 86, 2005, 309-348

[4] D. Ollis, P. Pichat and N. Serpone, TiO$_2$ photocatalysis – 25 years, Applied Catalysis B: Environmental, 99, 2010, 377-387

[5] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, Chem. Eng. J. 151,2009, 10-18

[6] P. Pichat, Ed. Photocatalysis and Water Purification: From Fundamentals to Recent Applications; Wiley-VCH Verlag GmbH and Co., 2013

[7] R.W. Matthews, Photooxidation of organic material in aqueous suspensions of titanium dioxide, Water Res. 20, 1986, 569-578

[8] S. Sakthivel, B. Neppolean, M. V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO$_2$, Solar Energy Materials and Solar Cells, 77, 2003, 65-82

[9] B. Pare, S.B. Jonnalagadda, H. Tomar, P. Singh, V.W. Bhagwat, ZnO assisted photocatalytic degradation of acridine orange in aqueous solution using visible irradiation, Desalination 234, 2008, 80-90

[10] K. Pirkanniemi, M. Sillanpaa, Heterogeneous water phase catalysis as an environmental application: a review, Chemosphere 48, 2002, 1047-1060

[11] S-M Lam, J-C Sin, A Z Abdullah, A R Mohamad, Degradation of wastewater containing organic dyes photocatalysed by ZnO: a review, Desalination and Water treatment 41,2012, 131-169

[12] Sindhu Joseph, K. P. Jyothi, S. P. Devipriya, Suguna Yesodharan, E.P. Yesodharan, Influence of reaction intermediates on the oscillation in the concentration of insitu formed hydrogen peroxide during the photocatalytic degradation of phenol pollutant in water on semiconductor oxides, Res. J. Recent Sci. 2 (2013) 82-89

[13] O. M. Shibin, B. Rajeev, Suguna Yesodharan, E. P. Yesodharan, ZnO photocatalysis using solar energy for the removal of trace amounts of α-methylstyrene, diquat and indigo carmine from water, *J Adv. Oxid. Technol.* 17,2014, 297-304

[14] B. Rajeev, Suguna Yesodharan, E. P. Yesodharan, Application of solar energy in wastewater treatment: Photocatalytic degradation of alpha-methylstyrene in water in presence of ZnO, *J Water Process Eng.* 8, 2015, 108-118

[15] R. J. Tayade, H. C. Bajaj, R. V. Jasra, Photocatalytic removal of organic contaminants from watrer exploiting tuned bandgap photocatalysts, *Desalination* 275, 2011, 160-165

[16] J. Yu, W. Wang, B. Cheng, B-L Su, Enhancement of photocatalytic activity of mesoporous TiO$_2$ powders by hydrothermal surface fluorination treatment, J Phys Chem. C. 113 (2009) 6743-6750

[17] C.S. Turchi and D.F. Ollis, Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack, J Catal. 122, 1990, 178-192

[18] B. Neppolian, H.C. Choi, S. Sakthivel, B. Aurobindo, B. Murugesan, Solar/UV induced photocatalytic degradation of three commercial textile dyes, J Hazard. Mater. 89, 2002, 303-317

[19] S. Anandan, A. Vinu, N. Venkatachalam, B. Arabindoo, V. Murugesan, Photocatalytic activity of ZnO impregnated Hβ and mechanical mix of ZnO/Hβ in the degradation of monocrotophos in aqueous solution, J Mol Catal. A: Chem. 256, 2006, 312-320

[20] S.G. Anju, Suguna Yesodharan, E.P. Yesodharan, Zinc oxide mediated sonophotocatalytic degradation of phenol in water, Chem. Eng. J. 189-190 (2012) 84-93

[21] S. Rabindranathan, S. Devipriya and S. Yesodharan, Photocatalytic degradation of phosphamidon on semiconductor oxides, J Hazard. Mater. 102 (2003) 217-229

[22] H.C. Yatmaz, A. Akyol, M. Bayramoglu, Kinetics of photocatalytic degradation of an Azo reactive dye in aqueous ZnO suspension, Ind. Eng. Chem Res. 43, 2004, 6035-6039

[23] K.E. O'Shea, I Garcia, M Aguilar, Titanium dioxide photocatalytic degradation of dimethyl and diethyl methylphosphonate: Effect of catalyst and environmental factors, Res. Chem. Intermed. 23,1997, 325-339

[24] S. Zhou, A.K. Ray, Kinetic studies for photocatalytic degradation of Eosin B on a thin film of Titanium dioxide, Ind. Eng. Chem. Res. 42, 2003), 6020-6033

[25] E. Evgenidou, K. Fytianos, I. Poulios, Semiconductor sensitised photodegradation of dichlorvos in water using TiO$_2$ and ZnO as catalysts, Appl. Catal B: Environ. 59 ,2005, 81-89

[26] J Poulios, I Tsachpinins Photodegradation of textile reactive black 5 in the presence of semiconducting oxides J Chem Technol. Biotechnol. 74, 1999, 39-357

[27] R. Comparelli, E. Fanizza, M.I. Curri, P.D. Cozzoli, G. Mascolo, A. Agostiano, UV induced photocatalytic degradation of azo dyes by organic capped ZnO nanocrystals immobilized onto substrate, Appl. Catal.B: Environ. 60,,2005, 1-11

[28] I. K. Konstantinou, Y. Deligiannakis, Effect of fumic acids and fulvic acids on the photocatalytic degradation of N diethyl-m-toluamide (DEET) using TiO$_2$ suspension and simulated sunlight in Functions of natural organic matter in changing environment, in 'Functions of Natural Organic Matters in Changing Environment' , Xu J, Wu J and He Y (Eds.) 2013, Springer Netherlands, pp 633-636

[29] J. Saien, A.R. Soleymani, Degradation and mineralization of Direct blue 71 in a circulating up-flow reactor by UV/TiO2 process and employing a new method in kinetic study, J Hazard. Mater. 14, 2007, 507-512

[30] T. Hirakawa, T. Daimon, M. Kitazawa, N. Ohguri, C. Koga, N. Negishi, S. Matsuzawa, Y. Nosaka, An approach to estimating photocatalytic activity of TiO$_2$ suspension by monitoring dissolved oxygen and superoxide ion on decomposing organic compounds, J Photochem. Photobiol. A: Chem. 190, 2007, 58-68

[31] W. S. Jenks, in Photocatalysis and water purification: From fundamentals to recent applications; P. Pichat, Ed., Wiley-VCH Verlag GmbH and Co.: 2013, pp 25-51

[32] S. Malato, J. Blanco, M I Maldonado, P. Fernandez-Ibanez, A. Campos, Optimizing solar photocatalytic mineralization pesticides by adding inorganic oxidizing species: Application to recycling of pesticide containers, Appl. Catal. B: Environ. 28 (2000) 163-174

[33] K. P. Jyothi, Suguna Yesodharan, E.P. Yesodharan, Ultrasound, Ultraviolet light and combination assisted semiconductor catalysed degradation of organic pollutants in water: Oscillation in the concentration of H$_2$O$_2$ formed insitu, Ultrason. Sonochem. 21 (2014) 1782-1796

[34] S. Malato, J. Blanco, M I Maldonado, P. Fernandez-Ibanez, A. Campos, Optimizing solar photocatalytic mineralization pesticides by adding inorganic oxidizing species: Application to recycling of pesticide containers, Appl. Catal. B: Environ. 28, 2000, 163-174

[35] D.D. Dionysiou, M.T. Suidan, I. Baudin, J-M Laine, effect of H$_2$O$_2$ on the destruction of organic contaminants – synergism and inhibition in a continuous mode photocatalytic reactor, Appl. Catal B: 50, 2004, 259-269