Green technology in wastewater treatment: Solar photocatalysis mediated by ZnO for the removal of trace amounts of carbendazim fungicide from water

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Abstract: *The photocatalytic degradation of trace amounts of carbendazim in water is investigated in presence of ZnO catalyst and solar energy. The degradation is very facile, leading to complete decolorisation of the dye within minutes. The chemical oxygen demand of the system also decreases with irradiation showing complete mineralization in less than 8 hr. The effects of various reaction parameters are investigated in detail and optimum conditions are identified. Most of the salts naturally found in water do not inhibit the degradation except PO_4^{3-} and Al^{3+}. Oxidants such as H_2O_2 and persulphate, which are known to enhance the photocatalytic degradation of many pollutants, have only limited enhancing effect in the case of solar ZnO photocatalytic degradation of carbendazim. Dissolved oxygen plays a significant role by serving as an electron scavenger and facilitating the formation of various reactive oxygen species. Some of the major intermediates formed during the degradation are also identified.*

Keywords: *Carbendazim, Photocatalysis, Green technology, Zinc oxide, Anions*

I.   Introduction

Extensive use of pesticides and other chemicals in agriculture is contaminating the natural water resources. Conventional methods of water treatment like adsorption, settling, floatation, filtration, chemical treatments etc. have limitations. These processes are only transferring the pollution from one medium to another and not transforming the pollutants to harmless compounds. In recent years, advanced oxidation processes (AOP) are investigated widely as potential efficient environment-friendly methods for the irreversible removal of toxic pollutants from contaminated water. Of these, semiconductor mediated heterogeneous photocatalysis is identified as an effective AOP for removal of wide variety of pollutants such as pesticides, petrochemicals, dyes etc. In many instances, the pollutants can be completely mineralized in to simple compounds like CO_2, water and salts [1-9]. Most commonly used semiconductor photocatalysts are TiO_2, ZnO and their modified forms in presence of UV, visible or sunlight. These oxides are relatively inexpensive, widely available and non-toxic. While TiO_2 is more stable against corrosion, ZnO has the added advantage of wider absorption in the solar wavelength.

Both TiO_2 and ZnO have comparable band gap energy (3.2 eV) and hence selection of one or the other depends on specific situations. Extensive investigations in our laboratories have shown that ZnO is more efficient for harnessing solar energy in wastewater treatment, especially when the process can be carried out in moderately acidic, alkaline or neutral pH range [8-10]. When a semiconductor is irradiated with light of wavelength greater than or equal to the band gap the valence band electrons are excited to the conduction band creating electron-hole pairs. The photogenerated electron-hole pairs can migrate to the catalyst surface or can recombine. The migrated species can initiate redox reactions leading to the formation of reactive free radicals. The electrons reduce the adsorbed oxygen to produce $O_2^{\cdot-}$ and the positively charged holes oxidize water to form OH radical. The OH radicals which are strong oxidants (E^o=2.8 V) can oxidize most of the organic pollutants [11-13]. Use of natural sunlight as the energy source for the photocatalytic reactions will make the process viable for commercial application. In this context, ZnO with wide absorption range in the solar spectrum is chosen for the current study aimed at developing an appropriate photocatalytic system for the removal of the fungicide pollutant carbendazim from water.

Carbendazim (methyl-1-H-benzimidazol-2-yl-carbamate) is a systemic benzimidazole fungicide, used as such as well as in combination with other fungicides such as triazoles, dithiocarbamates and dicarboximides. It is the active species of the commercial fungicides benomyl and thiophenate-methyl [14-16]. Carbendazim is extensively used world-wide. The annual production of active ingredient is over 12000 tones. Extensive usage of carbendazim results in contamination fresh water and its presence in natural water has been reported. It is relatively stable, having half-life of 6-25 weeks in water [17,18]. The chemical structure of carbendazim is given in Fig.1.
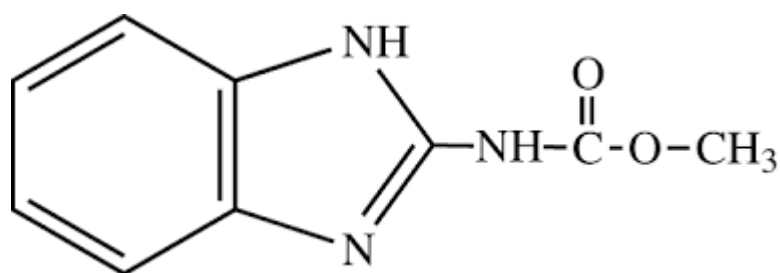
Few studies on the photodegradation of carbendazim in presence of UV light alone and in combination with TiO_2, ozone and H_2O_2 are reported [18, 19]. However, to the best of our knowledge, no investigations have been made so far on the application of solar energy or ZnO catalyst for the removal of carbendazim in traces from water. In this paper, we are reporting the results of our study on the solar photocatalytic degradation of carbendazim in water. Various process parameters affecting the degradation are evaluated in detail and optimum condition is identified. Some of the major reaction intermediates are also identified.

II. Materials and Methods

2.1. Chemicals and reagents

Carbendazim (99.9%) obtained from Sigma-Aldrich was used as such without further purification. Zinc oxide (BET surface area ~ 10 m^2/g) was from Merck Chemical Company (India). H_2O_2 and $Na_2S_2O_8$ (both LR grade) were from Nice chemicals India. Na_2SO_4, K_2SO_4, $CaSO_4$, $MgSO_4$, $Al_2(SO_4)_3$, NaCl, $NaNO_3$ and Na_2HPO_4 were from Merck Chemical Company (India). Terephthalic acid was from Rolex India. The solutions were prepared in Millipore water.

The solubility of carbendazim at 25°C is 8 mg/l. Saturated stock solution of carbendazim was prepared in Millipore water by stirring the required quantity at 60°C for 1 hr in a glass beaker. After cooling to room temperature the saturated solution is filtered through Whatmann filter paper 1. The clear solution is stable for two days.

The ZnO was characterized by XRD analysis (Bruker D2 Phaser) and SEM imaging (JEOL Model JSM-6390 LV) as given in Figures 2A and B respectively. The BET surface area and the pore size determination were done by Micrometrics Tristar surface area and porosity analyser. The average pore width is 123 Å. The hydrodynamic particle size as determined by Malvern mastersizer is ~3.2 μm.

2.2. Adsorption of carbendazim by ZnO

The adsorption of carbendazim by ZnO was determined by dispersing a fixed amount (0.1 g) of ZnO in 100 ml carbendazim solution of required concentration in a 250 ml reaction flask. The suspension was agitated continuously for 2 hours. The temperature was maintained at 29 ± 1°C. After 2 hours the suspension was kept undisturbed for 1 hr and then filtered through Millipore syringe filter 0.45μm. The concentration of carbendazim remaining in the supernatant was determined using spectrophotometer. No significant change in concentration was observed by keeping the suspension overnight indicating that 2 hour is sufficient for maximum adsorption.
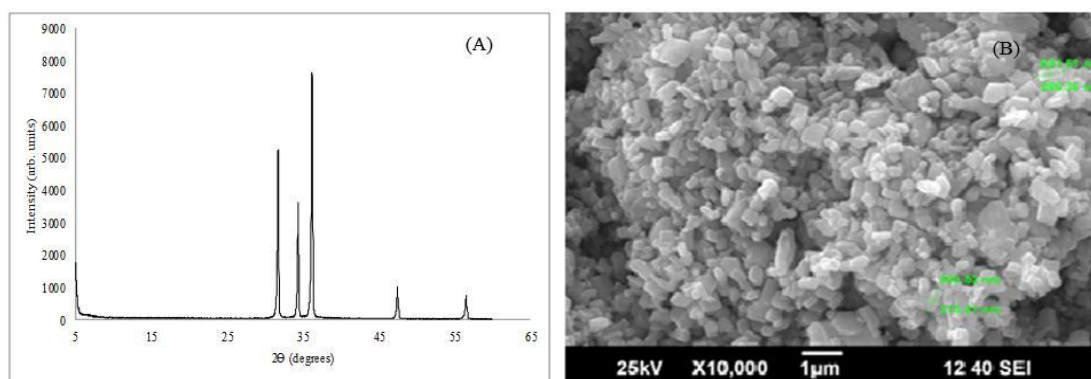

Figure 2: (A) XRD of ZnO (B) SEM image of ZnO.

The adsorption was calculated by using the equation.

$$q_e = (C_0 - C_e)V/W \qquad (1)$$

where q_e is the quantity adsorbed in mg/g of the adsorbent, i.e. adsorption capacity, 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 (L) and W is the mass of the adsorbent in gram.

The same procedure was used for measuring the adsorption of various ions by using respective salt solutions under required conditions.   The anion and cation concentration before and after adsorption was determined by ion chromatography and ICP-MS respectively.

2.3. Photocatalytic degradation of carbendazim by ZnO under solar light

Photocatalytic experiments in presence of sunlight were performed using a jacketed pyrex reactor. The carbendazim solution (50 ml) together with ZnO was taken in the inner compartment. Cooling water from a thermostat (29 ± 1^oC) was continuously circulated through the outer jacket. Solar experiments were performed by placing the reaction 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 February-May, September-October 2013 and February-May, September-October 2014. The average intensity of solar light during the experiments was 1.25×10^5 Lux, as calculated from the measurements using Digital Lux meter (LT-Lutron LX-101A). The suspension was stirred frequently to ensure uniform mixing. Samples were drawn at regular intervals, filtered through 0.45μm filter and analyzed for the carbendazim concentration by Spectrophotometry (284 nm). Suspension prepared and kept under identical conditions in the dark was used as the reference in each case to eliminate the contribution from adsorption and dark reaction.

2.4. Analysis of reaction products/intermediates

The degradation of carbendazim during reaction was followed by spectrophotometry (284 nm) using a Perkin-Elmer Lambda 650 Spectrophotometer. The absorption maximum of carbendazim changes with pH of the solution [19,20]. This was also considered during the analysis. The reaction intermediates were identified by using Agilant 6460 Triple quad LC-MS equipped with an ESI interface operating in positive polarity mode. The LC column was C18 of 150 mm x 4.6 mm and 5μm particles (Phenomenex). The mobile phase was acetonitrile - formic acid (0.1%) in the ratio 20:80. The scanning was done by multiple reactions monitoring (MRM) in the range of 50-250 amu.

2.5. Detection of hydroxyl radicals

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 [21,22]. 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. The hydroxyl radical formation in presence of cations and anions is monitored by adding 20 ml (8 mg/l) respective ion salt solutions to the ZnO and stirring it for 10 minutes before adding TPA solution. After adding TPA to the suspension, whole system is irradiated with sunlight for 10 minutes and recorded the PL spectrum as mentioned.

III.   Result and discussion

Preliminary investigations on the solar photocatalytic degradation of carbendazim (7mg/l) using zinc oxide (0.1g/l)   as catalyst showed that the process is very efficient and ~ 80% degradation occurred in 30 minutes at the natural pH (5.5) of the solution. Adsorption studies showed practically negligible adsorption of carbendazim on the surface of ZnO. No degradation was observed in parallel experiments conducted in presence of sunlight and in dark with/without catalyst. This showed that both sunlight and ZnO are essential to effect the degradation of carbendazim. Various parameters relevant for the degradation of the pollutant are optimized as follows:

3.1. Effect of catalyst dosage

The catalyst loading is known to influence the rate of the semiconductor mediated photocatalytic reaction in aqueous phase. The optimum catalyst loading for a particular system depends on a number of parameters such as concentration of substrate species, area/volume ratio of the photoreactor and the intensity of the light used [1, 23]. The effect of catalyst loading on the rate of degradation of carbendazim, keeping all other parameters constant is shown in figure 3.
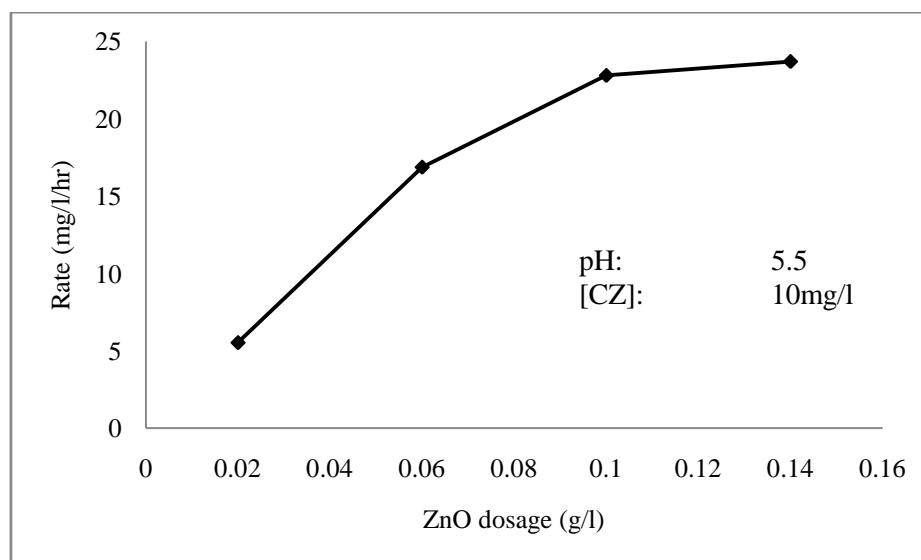

Figure 3: Effect of catalyst dosage on the rate of degradation of carbendazim.

With increase in catalyst loading, the reaction rate also increases, reaches an optimum at 0.1g/l and stabilises thereafter. The increase in reaction rate is directly proportional to the number of active sites which increases with the catalyst loading. At higher loadings the effective absorption of light will be better and this leads to the generation of more reactive oxygen species (ROS) such as OH radical and enhanced degradation. However, beyond the optimum, any further increase in the catalyst loading will hinder the light penetration by scattering. The increased opacity of the suspension masks the effective absorption of light by ZnO surface. Other factors that can affect the photocatalytic efficiency at higher ZnO loading include; particle aggregation and deactivation of the photoactive ZnO by collision with ground state molecules [8-10]. The optimum concentration identified here, i.e. 0.1 g/l, was used for all other studies, unless indicated otherwise.

3.2. Effect of initial concentration of carbendzim, Kinetics

The photocatalytic degradation rate of organic molecules in aqueous medium varies with the initial concentration. This is verified in the present context by varying the initial concentration of carbendazim from 3-10 mg/l under otherwise identical reaction conditions. The percentage degradation of carbendazim decreases as the concentration is increased. The rate of degradation increases with increase in concentration upto 7 mg/L and stabilizes thereafter (Figure 4).
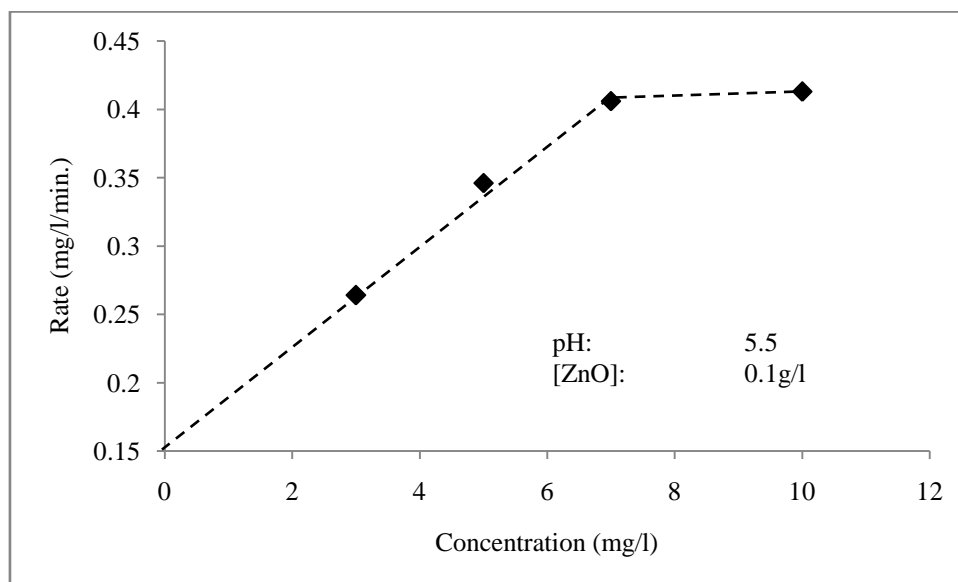
Figure 4: Effect of concentration of carbendazim on the rate of degradation.

The optimum degradation rate attained is ~25.4 mg/l/hr. The results clearly show that the degradation follows variable kinetics, with pseudo first order at lower concentration (3-7 mg/l) and zero order at higher concentration (> 7 mg/L). This kinetics is reported in many other cases [24-26]. The pseudo first order kinetics is rationalized in terms of the modified Langmuir-Hinshelwood model (L-H model) which accommodates the reactions occurring at solid-liquid interface as well. The applicability of the model is based on the assumptions that reaction is in dynamic equilibrium and there is no competition between the substrate and the reaction intermediates for the surface sites as well as the ROS. The simplest L-H kinetic model applicable to photocatalytic degradation of chemical contaminants may be proposed as follows [27-30].

$r_0 = -dC/dt = kKC_0/(1 + KC_0)$ (2)   where

r_0 = initial rate of degradation of the contaminant (mg/L/min)

C_0 = initial concentration of the contaminant (mg/L)

C = concentration (mg/L) remaining after time t.

t = irradiation time (minutes)

k = limiting reaction rate at maximum coverage for the experimental conditions (min^{-1}) and

K = equilibrium adsorption constant of the contaminant

At higher concentration of the substrate / when the concentration is more than the saturation coverage for the surface of the catalyst, i.e. $KC_0 \gg 1$, the equation simplifies to zero order rate equation as

$-dC/dt = k$ (3)

When the concentration of the contaminant is very small ($KC_0 \ll 1$), the equation can be simplified as

$-dC/dt = kKC_0 = k'C_0$ (4)   where k' is the pseudo first order rate constant.

Rearranging and integrating the above equation yields a typical pseudo first order model as follows:

$C = C_0 e^{-k't}$ (5)

$\ln(C_0/C) = k't$ (6)

Plot of $\ln(C_0/C)$ vs t will yield straight line for first order reactions. The slope of the straight line will be the pseudo first order rate constant.

The half-life ($t_{1/2}$), the time required for 50% degradation is calculated by replacing the C by $C_0/2$ and t by $t_{1/2}$ in the Eq. (6) [30]:

$t_{1/2} = \ln2/k = 0.693/k$ (7)

The plot of $\ln(C_0/C)$ vs t for the photocatalytic degradation of carbendazim at selected concentrations are shown in the figure 5. The linearity of the plot confirms that the degradation fits well with the L-H model for the pseudo first order kinetics. The calculated value for the pseudo first order rate constants are given in the table1.
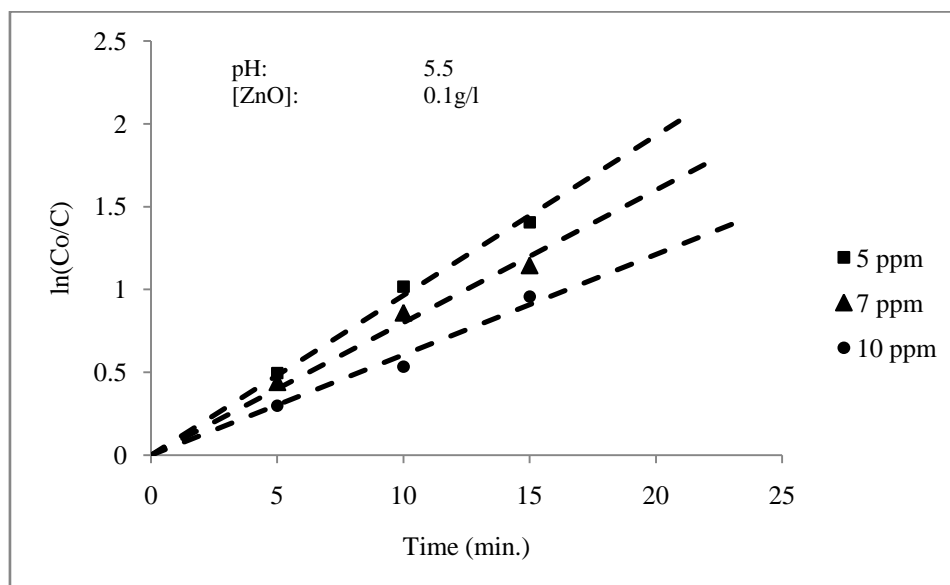
Figure 5: Logarithmic plot of pseudo first order kinetics for the degradation of carbendazim.

Table 1

Pseudo first order rate constants for the photocatalytic degradation of carbendazim over ZnO

pH = 5.5 Temp: 29 ± 1 °C

Experiment	ZnO (g/l)	Carbendazim (mg/l)	k' x10^{-2} min^{-1}	t$_{1/2}$ min
1	0.1	5	9.08	7.62
2	0.1	7	7.04	9.84
3	0.1	10	6.57	10.54

It is evident that the value of *k'* decreases as the concentration of carbendazim is increased. For a particular amount of catalyst loading the active surface sites and the reactive species generated will be constant. At the same time the number of substrate molecule increases as the concentration increases. The effective interaction between the substrate and the reactive species generated will be finite. The relative percentage fraction of interacting substrate will be less at higher concentrations and this leads to the lowering of the rate constant with concentration.

The $t_{1/2}$ for the reaction in the selected concentration range increases with concentration, which is expected since the reaction rate constant decreases as the concentration is increased.

Rearranging equation (2) yields equation 8 as follows:

$$1/r_0 = (1/kKC_0) + 1/k \qquad (8)$$

Based on this, the validity of L-H model can be reconfirmed by the linearity of the inverse plot, $1/r_0$ vs $1/C_0$. Figure 6 shows excellent linearity in the selected concentration range thereby reconfirming the pseudo first order kinetics in the present instance. The values of *k* and *K* can be calculated from the slope of the straight line and from the intercept respectively based on equation (8) [28,29]. At higher concentration, the substrate as well as the intermediates formed may absorb some of the incident photons thereby reducing the availability of light for the activation of ZnO. Also it is possible that the higher concentration of intermediates formed from the higher concentration of substrate may get adsorbed or loosely attached to the ZnO surface and thus hinder the approach of reactant to the active site. However, the optimum concentration of 7 mg/l is applicable only under the present conditions. The optimum will be different under a different set of experimental condition such as light intensity, catalyst loading and reactor size and geometry etc. For every set of reaction conditions, respective parameters have to be optimized.
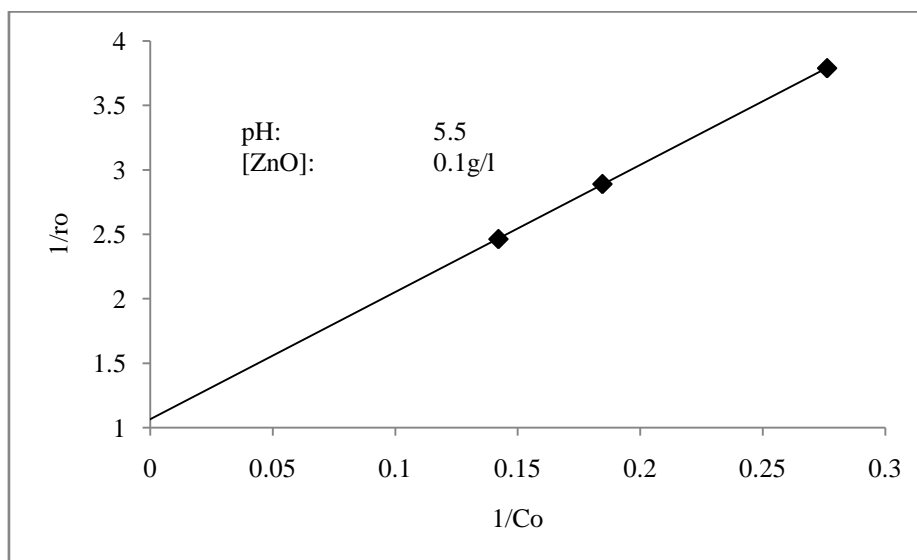
Figure 6: Reciprocal plot of initial rate of degradation of carbendazim versus initial concentration.

3.3. Effect of pH on the degradation

The pH of the aqueous medium has significant role in the semiconductor mediated photocatalytic degradation reactions. The surface characteristics of the semiconductors changes with the pH of the dispersing medium. For semiconductors, the net electric charge on the surface in aqueous medium is characterized in terms of point of zero charge (PZC). The surface is positively charged below the PZC while it will be negatively charged above [26,32]. The PZC of ZnO is approx.9.0. Since the catalytic reactions are surface mediated, the net charge on the surface has important role in accommodating the reactant species in the catalyst surface and also directly contributes to the rate of the reaction. In aqueous medium, depending on the pH, carbendazim exists in protonated (pH< p*Ka~4.2*) or in neutral form (pH> p*Ka*). Transformation of carbendazim to aminobenzimidazole at higher pH ranges has also been reported [15]. Parallel studies conducted in the dark without catalyst in the pH range 3-11 showed no change in the carbendazim concentration. The effect of pH on the photocatalytic degradation of carbendazim is studied by varying the pH of the solution while other reaction parameters are kept constant. The results are plotted in figure.7. The degradation increases with increase in the solution pH and reaches maximum at pH 5. The degradation remains steady from pH 6 to 9 and decreases at pH > 9. The lower degradation at pH< 4 may be due to ZnO corrosion and consequent decrease in the amount of catalyst. Similar results are reported in the case of ZnO-mediated photocatalytic degradation of diquat also [32]. Below the p*Ka* value *of 4.2,* carbendazim exists in the protonated form. Similarly, below the PZC of ~9.0, the surface of ZnO is positively charged. The electrostatic repulsion between the protonated form
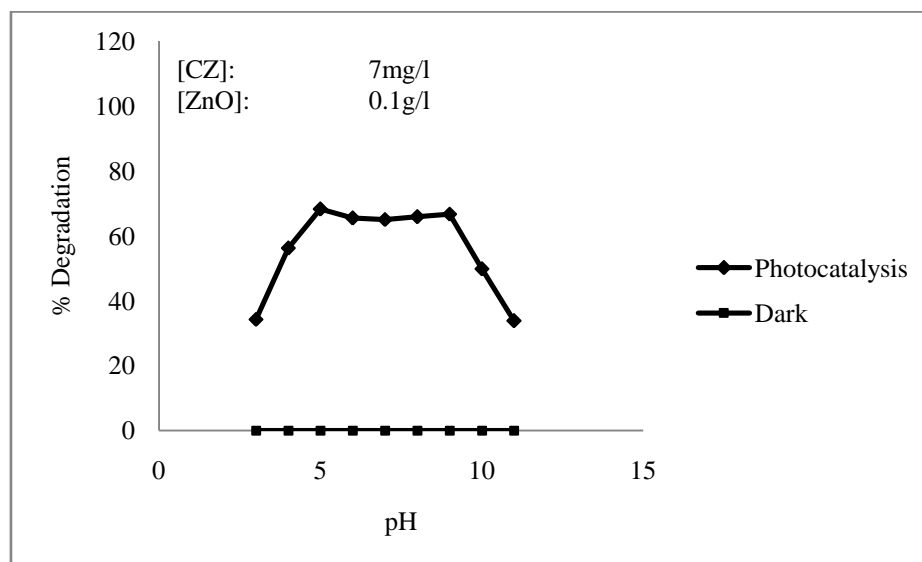
Figure 7: Effect of pH on the degradation of carbendazim.

of carbendazim and the positively charged surface of ZnO may be another reason for the low degradation rate at pH < 4.2. Above pH 4.2 carbendazim in the neutral form can access or be in proximity to the surface which contributes to the increase in the percentage degradation at higher pH. However, it is observed that the adsorption of carbendazim on ZnO is negligible at all pH. Hence the interaction between the ROS and carbendazim occurs in the bulk or nearer to the ZnO surface.

At alkaline pH > 9, the ZnO is negatively charged and once again the repulsion of carbendazim from the surface leads to decreased degradation. The possibility of alkaline dissolution of ZnO as in reaction 9 also cannot be ruled out..

$$ZnO + H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-} \qquad (9)$$

Since the degradation remains at the optimum at the natural pH of the reaction suspension, i.e. 5.5, all further studies are carried out without adjustment of the pH, unless indicated otherwise.

3.4. Effect of oxidants

The photocatalytic degradation rates of many organic pollutants in aqueous medium is enhanced by the addition of certain oxidants. They can act as electron scavengers thereby preventing the electron-hole recombination. H_2O_2, ozone and $S_2O_8^{2-}$ have been reported to accelerate the photocatalytic degradation of organic pollutants in aqueous medium[8,16,19,24,33]. The degradation proceeds *via* ˙OH radical formed during the irradiation. Combination of H_2O_2 with semiconductor oxides leads to enhancement in the degradation of many pollutants [8,9,24,32]. H_2O_2 is formed as an intermediate in many photocatalytic reactions. Recently Jyothi et al [34] demonstrated the concurrent formation and decomposition of *in-situ* formed H_2O_2 leading to oscillation in its concentration. Formation of H_2O_2 is observed in the current instance also. However, the H_2O_2 increases with the degradation of carbendazim and eventually stabilises and increases again. The stabilization occurs when the rates of formation and decomposition balance each other, especially towards the later stages of degradation. However, once the degradation of carbandazim to various intermediates is over, the latter will begin to be degraded and eventually mineralized resulting in another increase in the concentration of H_2O_2 (Figure 8).
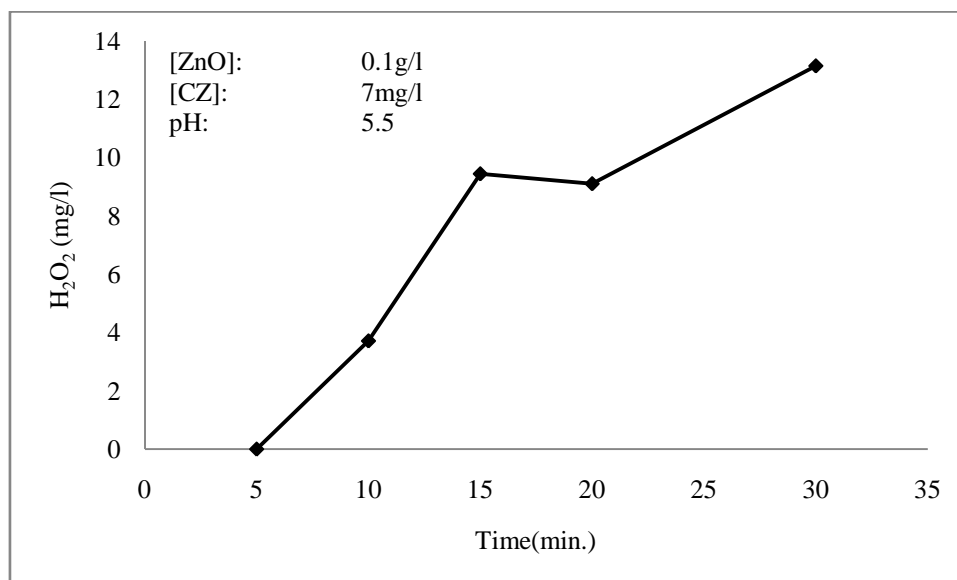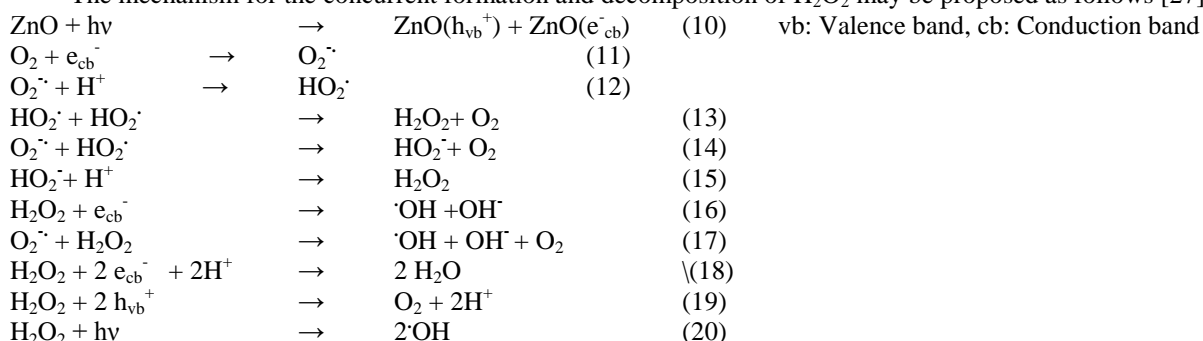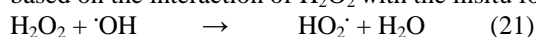
Figure 8: Formation of H_2O_2 during the photocatalytic degradation of carbendazim.

The mechanism for the concurrent formation and decomposition of H_2O_2 may be proposed as follows [27]:

$ZnO + h\nu \quad\quad\quad \rightarrow \quad\quad ZnO(h_{vb}^+) + ZnO(e_{cb}^-) \quad (10) \quad\quad$ vb: Valence band, cb: Conduction band

$O_2 + e_{cb}^- \quad\quad \rightarrow \quad O_2^{\cdot-} \quad\quad\quad\quad (11)$

$O_2^{\cdot-} + H^+ \quad\quad \rightarrow \quad HO_2^{\cdot} \quad\quad\quad\quad (12)$

$HO_2^{\cdot} + HO_2^{\cdot} \quad\quad \rightarrow \quad H_2O_2 + O_2 \quad\quad (13)$

$O_2^{\cdot-} + HO_2^{\cdot} \quad\quad \rightarrow \quad HO_2^- + O_2 \quad\quad (14)$

$HO_2^- + H^+ \quad\quad \rightarrow \quad H_2O_2 \quad\quad\quad\quad (15)$

$H_2O_2 + e_{cb}^- \quad\quad \rightarrow \quad {\cdot}OH + OH^- \quad\quad (16)$

$O_2^{\cdot-} + H_2O_2 \quad\quad \rightarrow \quad {\cdot}OH + OH^- + O_2 \quad (17)$

$H_2O_2 + 2 e_{cb}^- + 2H^+ \quad \rightarrow \quad 2 H_2O \quad\quad\quad\quad \backslash(18)$

$H_2O_2 + 2 h_{vb}^+ \quad\quad \rightarrow \quad O_2 + 2H^+ \quad\quad (19)$

$H_2O_2 + h\nu \quad\quad \rightarrow \quad 2{\cdot}OH \quad\quad\quad\quad (20)$

Since H_2O_2 is a good oxidant by itself and also good electron scavenger, addition of small amount of H_2O_2 is expected to influence the degradation of carbendazim. This possibility is investigated with the addition of small quantity (1, 4 and 8 ppm) of H_2O_2 to the photocatalytic reaction system. Enhancement in the degradation of carbendazim is observed in all cases (figure 9). Effect of increase in the concentration of H_2O_2 on the percentage degradation is negligible with only slight enhancement. This may be because, the insitu formed H_2O_2 has already played the enhancing role and the extra addition results in concurrent decomposition and reformation of H_2O_2 without any specific effect on the degradation of carbendazim. This may be explained based on the interaction of H_2O_2 with the insitu formed highly reactive ${\cdot}OH$ radicals as follows:

$H_2O_2 + {\cdot}OH \quad\quad \rightarrow \quad HO_2^{\cdot} + H_2O \quad\quad (21)$

$HO_2^{\cdot} + {\cdot}OH \quad\quad \rightarrow \quad H_2O + O_2 \quad\quad (22)$

Comparing with ${\cdot}OH$ radical $HO_2^{\cdot}$ is a weak oxidant [32]. The added H_2O_2 can also absorb sunlight and undergo self-photolysis which reduces the amount of incident radiation for the activation of ZnO. Since the population of H_2O_2 in the bulk and also in the vicinity catalyst is more at higher concentrations, the photo-generated ${\cdot}OH$ radical can easily react with the former than with carbendazim molecule. The overall effect of these factors limit the enhancement in the degradation of carbendazim by added H_2O_2. This explains the 'nil' effect in the case of added H_2O_2 at relatively higher concentration.
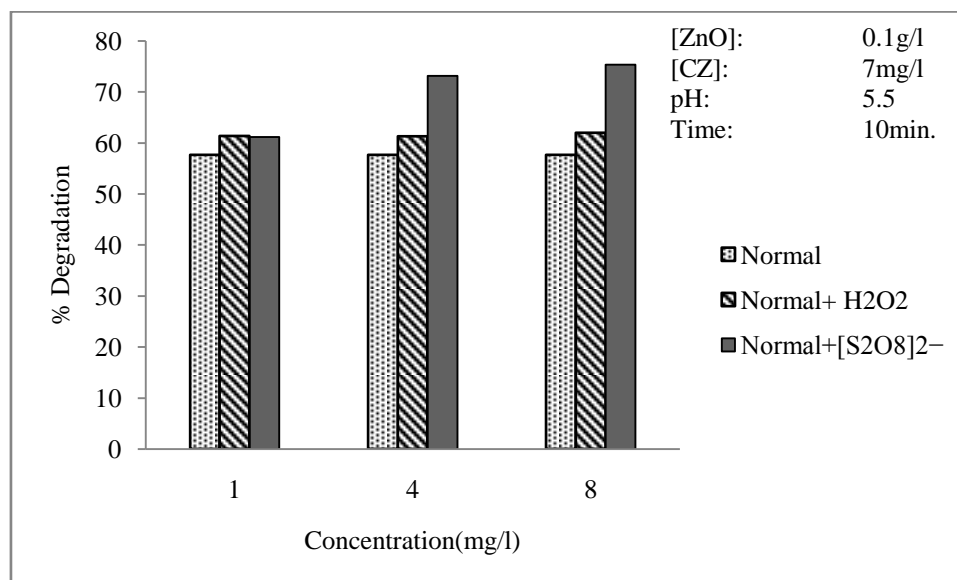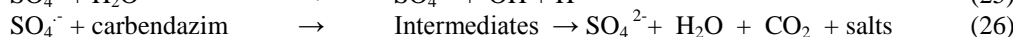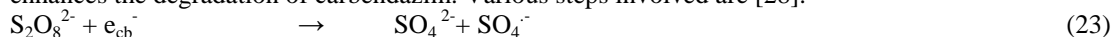
Figure 9: Effect of H_2O_2 and persulphate on the photocatalytic degradation of carbendazim.

In this context, the effect of persulphate (PS) on the photocatalytic degradation of carbendazim also is investigated using the sodium salt, i.e. $Na_2S_2O_8$. The results are shown in Figure 9. The degradation is enhanced by about 20%. Unlike in the case of UV/PS, in the case of direct sunlight, the enhancement is less probably because PS is not fully activated by the latter. The enhancing effect of PS is attributed to the electron scavenging ability thereby reducing the electron hole recombination as in the case of H_2O_2. It also produces very strong oxidants such as sulfate radicals (E^o= 2.6 V) [30] which can interact directly with carbendazim and oxidise it. Further the $SO_4^{·-}$ radicals can interact with H_2O generating equally reactive $^·OH$ radicals which also enhances the degradation of carbendazim. Various steps involved are [28]:

$$S_2O_8^{2-} + e_{cb}^- \quad \rightarrow \quad SO_4^{2-} + SO_4^{·-} \tag{23}$$
$$SO_4^{·-} + e_{cb}^- \quad \rightarrow \quad SO_4^{2-} \tag{24}$$
$$SO_4^{·-} + H_2O \quad \rightarrow \quad SO_4^{2-} + {}^·OH + H^+ \tag{25}$$
$$SO_4^{·-} + carbendazim \quad \rightarrow \quad Intermediates \rightarrow SO_4^{2-} + H_2O + CO_2 + salts \tag{26}$$

The enhancement by the oxidants is relatively less in both cases probably due to the inadequacy of sunlight to activate them compared to UV light or other sources.

3.5. Effect of anions and cations

Natural water contains considerable amount of different types of dissolved salts. 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 affect the photocatalytic degradation in many ways, most important being the competitive adsorption on the active surface sites. This will prevent the pollutant molecules from adsorption and activation. Other effects include; reducing the solar radiation reaching the catalyst surface, deactivation of the ROS, unwanted byproducts which may influence the efficiency of photocatalysis and mineralization etc. [8, 26, 31,35,36]. Factors such as pH, nature of catalyst, substrate, concentration of ionic species etc also influence the nature of anion effect on the photocatalytic efficiency.

The effect of salts on the degradation is evaluated both in terms of anions and cations. The effect of the anions, Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} on the degradation is evaluated at various concentrations keeping the cation the same, i.e. Na^+ (Figure 10).
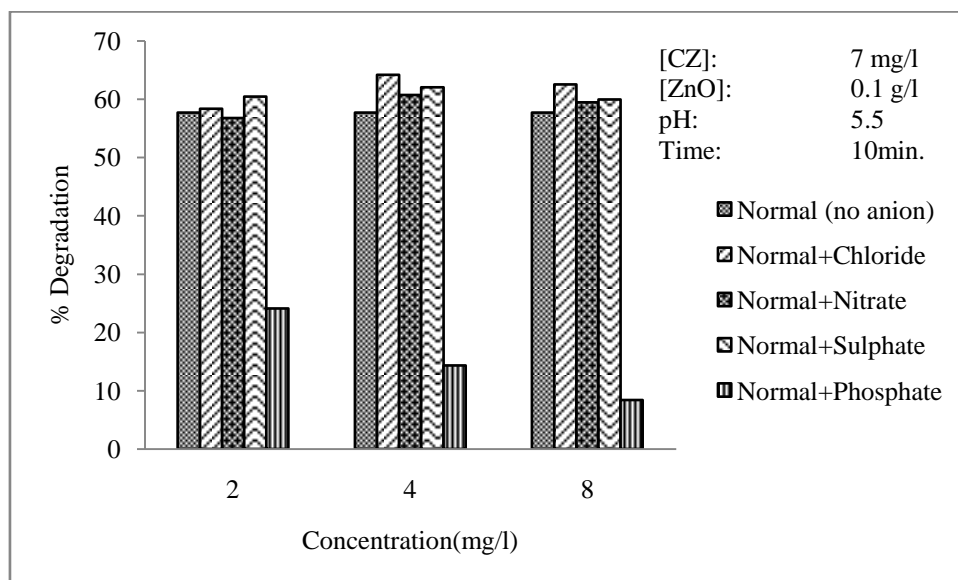
Figure 10: Effect of anions on the photocatalytic degradation of carbendazim [Cation:Na^+].

Similarly, the effect of cations Na^+, K^+, Ca^{2+}, Mg^{2+} and Al^{3+} is evaluated keeping the anion the same, i.e. SO_4^{2-} (Figure 11). As the results show, the anions, except PO_4^{3-}, at the concentrations tested here have no effect on the degradation of carbendazim. Similarly, except in the case of Al^{3+}, other cations do not have any significant effect on the degradation.
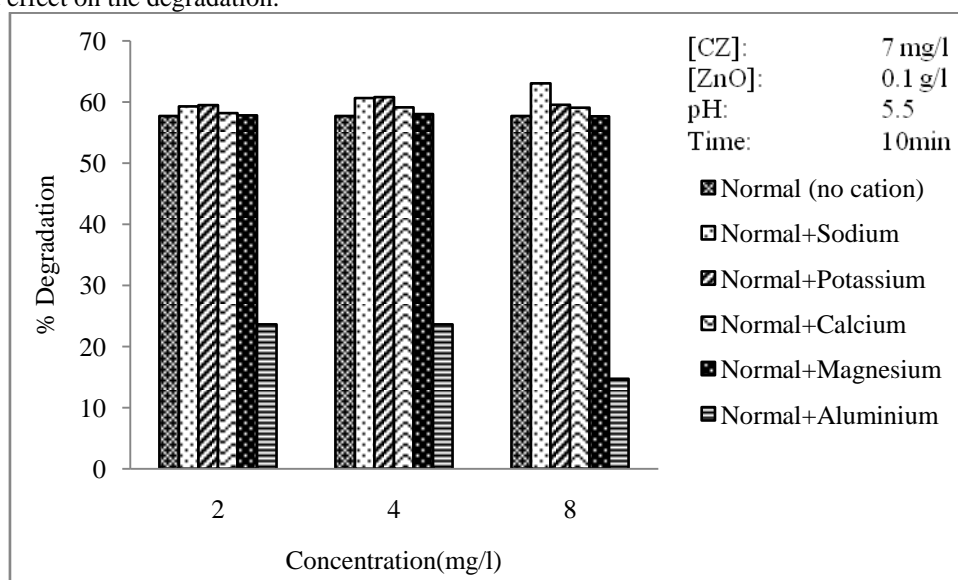

Figure 11: Effect of cations on the photocatalytic degradation of carbendazim (Anion:SO_4^{2-}).

Except for phosphate, other anions tested here have no effect on the degradation, at least in the concentration range of 2-8 mg/L. The detrimental effects of HPO_4^{2-} on the photocatalytic degradation has been reported in the case of both ZnO and TiO_2 catalysts [37]. Preferential adsorption by PO_4^{3-} as the possible cause of inhibition is tested by measuring the adsorption of various anions on ZnO. Since the sodium salt used as the source of the anions, the concentration of Na in the solution also is monitored. It is observed that HPO_4^{2-} is getting preferentially adsorbed on to the ZnO while the adsorption of other anions is practically negligible. The adsorbed HPO_4^{2-} can block the active surface sites from the incident radiation. It can also scavenge the ·OH radical generated insitu. Quantification of ·OH radicals by the TPA procedure described in Section 2 shows that in the presence of HPO_4^{2-} the relative concentration of the radicals is much less (Figure12).
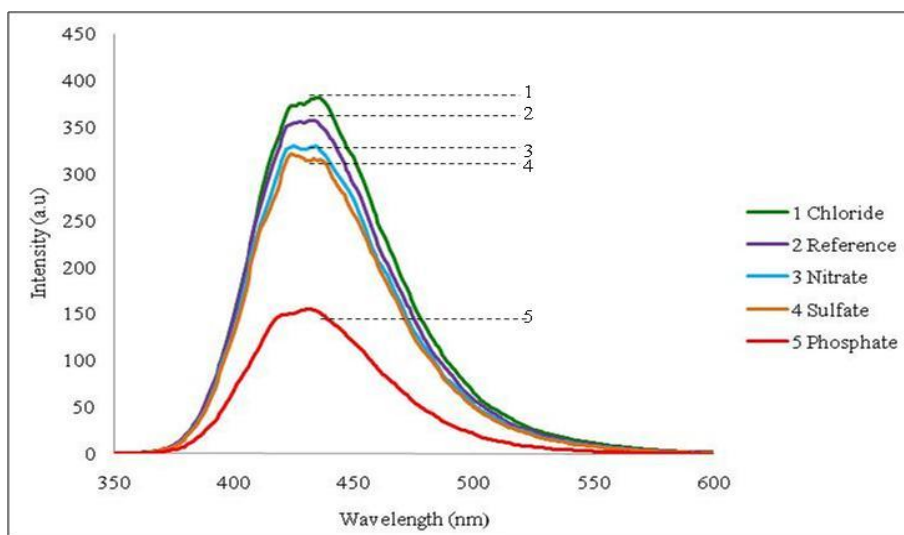
Figure 12: PL spectral changes observed in the photocatalytic system in presence of various anions.

The intensity of photoluminescence spectrum of the 2-hydroxyTPA formed during the experiments is proportional to the ˙OH radical generated [21,22]. The intensity remains more or less similar in the absence as well as presence of all other anions indicating that they do not scavenge the ˙OH radicals. In the case of different cations (anion SO_4^{2-} is constant), the ˙OH scavenging is negligible except Al^{3+} which inhibits the formation of ˙OH significantly, as seen in Figure13. The results clearly show that the inhibition caused by anions and cations is due to the detrimental effect on surface initiated processes and resulting decrease in the availability of ˙OH radicals. Even those ˙OH radicals formed insitu also get competitively scavenged by the ions whereby they are less available for the degradation of the substrate carbendazim.
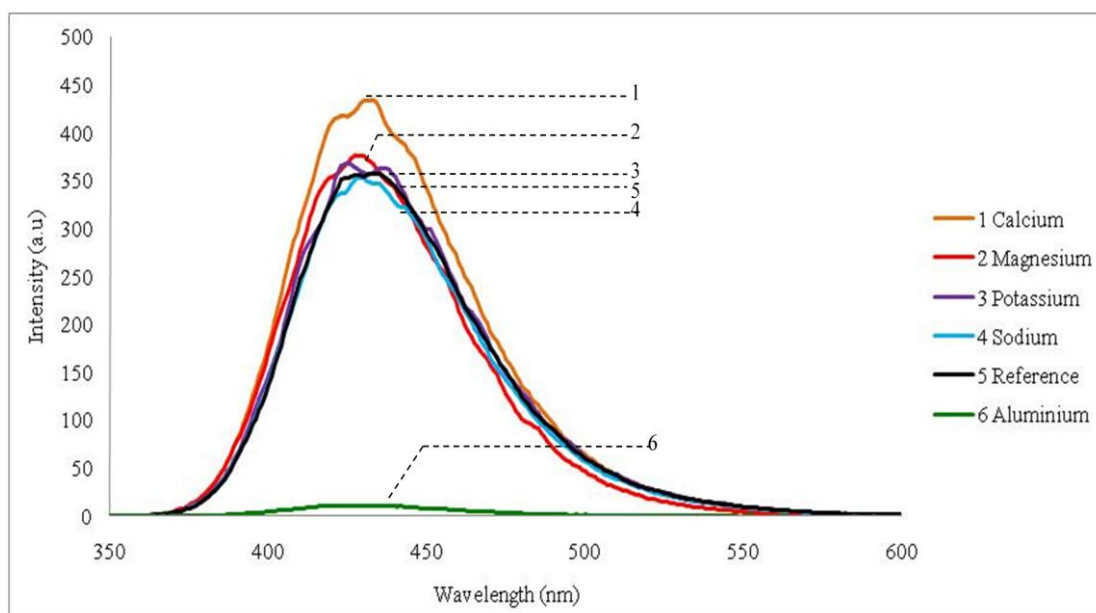

Figure 13: PL spectral changes observed in the photocatalytic system in presence of various cations.

3.6. Effect of oxygen.

Dissolved oxygen in reaction medium is a key factor for semiconductor mediated photocatalytic reactions. Dissolved oxygen is a good electron scavenger that can prevent the recombination of photogenerated hole/electron pair [23]. Further the electron scavenging by oxygen generates superoxide radicals which facilitate the formation of other reactive species. To confirm the effect of dissolved oxygen on the photocatalytic

degradation of carbendazim, the reaction medium is deaerated with N_2 and the experiments are carried out under identical optimized conditions. As shown in the figure 14 the percentage degradation of carbendazim in much less in the deaerated system. The relatively smaller percentage degradation may be effected by the adsorbed surface oxygen and small fraction of dissolved oxygen that cannot be removed by N_2 deaeration. The decrease in the percentage degradation of carbendazim with time in the deaerated system clearly indicates that once the remaining oxygen has been fully consumed; the reaction will not proceed further. Similar results were reported in the case of the photocatalytic degradation of diquat also [32].
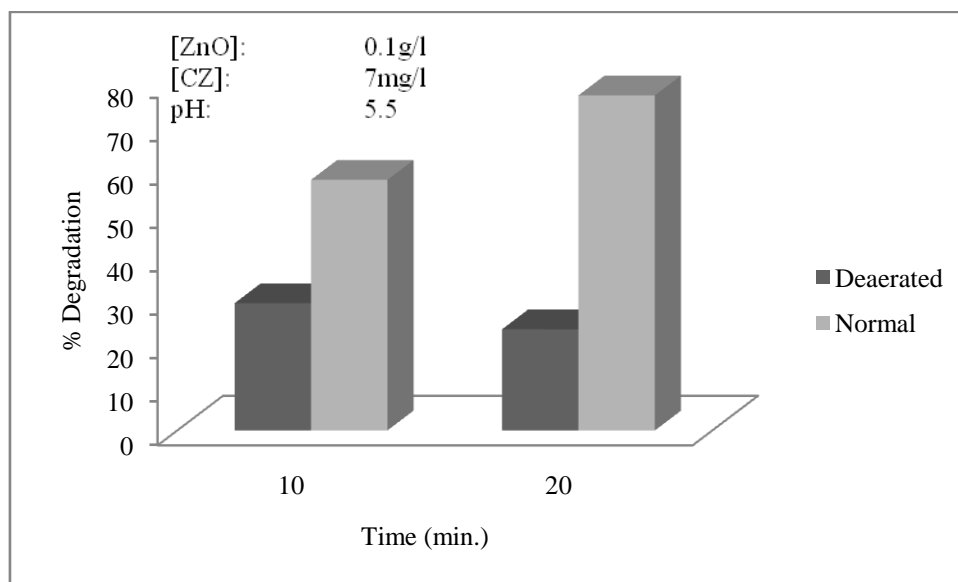

Figure 14: Effect of deaeration with N_2 on the photocatalytic degradation of carbendazim.

IV.   Identification of reaction intermediates

The reaction intermediates have been identified by LC/MS. The reaction system at two different stages, i.e. 50% and 80% is chosen for the purpose. The mass spectra at these two conditions are shown in figures 15A and B.
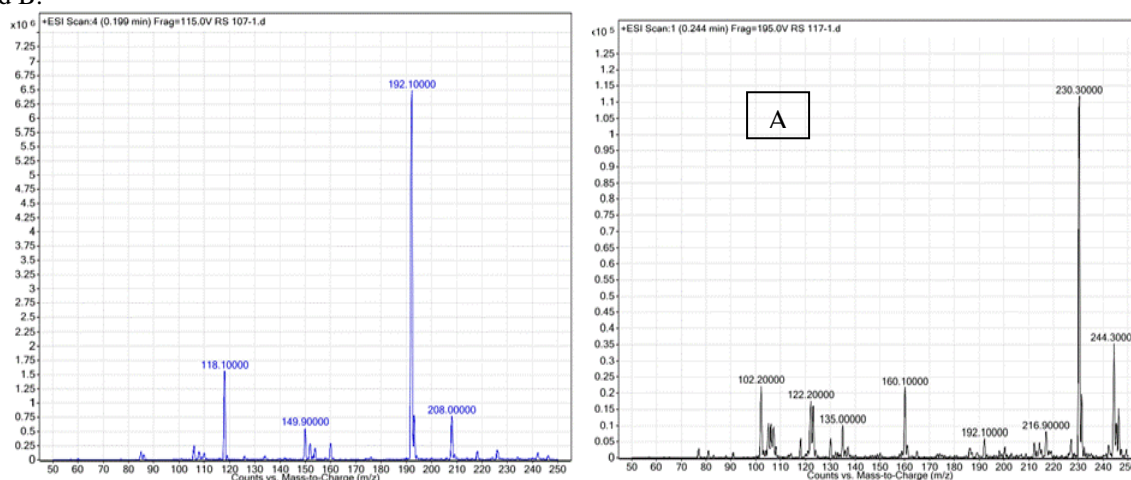

Figure 15: Mass spectra of degradation products, (A) 50% degradation, (B) 80% degradation.

Various intermediates identified are shown in Table 2. The presence of intermediates like protonated carbendazim with added hydroxyl group (m/z =208) confirms reaction between the substrate molecule and the OH radicals formed insitu. Comparing the mass spectrums at two different stages of reaction confirms the disappearance of certain intermediates and the formation of lower molecular mass species.

Table.2
Possible intermediates formed during the solar photocatalytic degradation of carbendazim.

Molecular or Cationic mass	Intermediates/Reaction products
208	
160	
149	
135	
118	
192	
	Carbendazim

Decrease in chemical oxygen demand (COD) also confirms the fragmentation of various intermediates and eventual mineralization. The COD at different times of irradiation is shown in the figure16. Complete mineralization of carbendazim achieved in presence of sunlight in 8 hr.
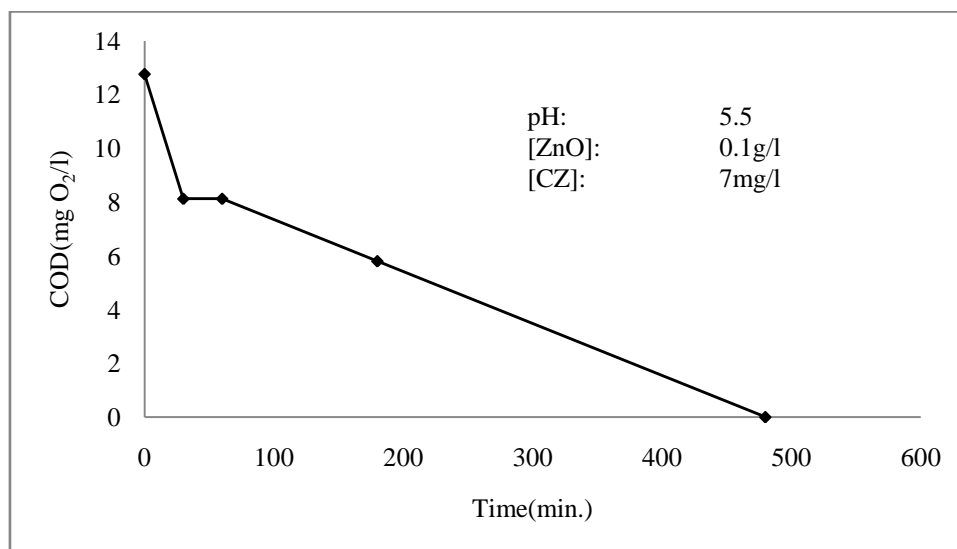
Figure 16: COD of the reaction system after different periods of irradiation.

V.   Conclusion

The photocatalytic degradation of trace amounts of carbendazim in water is investigated in presence of ZnO catalyst and solar energy. The degradation is very facile, leading to complete decolorisation of the dye within minutes. The chemical oxygen demand of the system also decreases with irradiation showing complete mineralization in less than 8 hr. The effects of various reaction parameters are investigated in detail and optimum conditions are identified. Most of the salts naturally found in water do not inhibit the degradation except PO_4^{3-} and Al^{3+}. Oxidants such as H_2O_2 and persulphate, which are known to enhance the photocatalytic degradation of many pollutants, have only limited enhancing effect in the case of solar ZnO photocatalytic degradation of carbendazim. Dissolved oxygen plays a significant role by serving as an electron scavenger and facilitating the formation of various reactive oxygen species. Some of the major intermediates formed during the degradation are also identified.

Acknowledgement

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