3.1 Abstract

Semiconductor mediated hydrogen peroxide-assisted photocatalytic degradation of three selected pesticide derivatives, Bentazon (1), Chloramben (2) and Cyanazine (3) has been investigated in aqueous suspensions under a variety of conditions. The degradation was studied by monitoring the depletion in total organic carbon (TOC) content and decrease in substrate concentration as a function of irradiation time. The degradation kinetics was investigated under different conditions such as the type of TiO₂ (Anatase/Anatase-Rutile mixture), reaction pH, catalyst dosage and hydrogen peroxide (H₂O₂) concentration. The degradation rates were found to be strongly influenced by all the above parameters. Titanium dioxide Degussa P25 was found to be more efficient as compared with other two commercially available TiO₂ powders like Hombikat UV100 and PC500 from Millennium Inorganic Chemicals. GC-MS analyses of the irradiated mixture of these pesticides indicate the formation of several intermediate products which have been characterized on the basis of molecular ion/mass fragmentation pattern and also on comparison with the NIST library. Plausible mechanisms for the formation of different products during photocatalytic treatment of pesticide derivatives 1-3 in the presence of TiO₂ have been proposed. The use of H₂O₂ substantially increased the efficiency of TiO₂ photocatalytic degradation.
3.2 Introduction

The intensive use of pesticides in agricultural practice frequently gives rise to the contamination of soil and water resources. Due to the toxicity, stability to natural decomposition and persistence in the environment, these compounds have been the cause of much concern to the societies and regulating authorities around the world. The remediation of toxic compounds from ground water supplies has been a great interest by the scientific communities. During the past two decades, photocatalytic processes involving TiO$_2$ semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the degradation of organic pollutants in aqueous suspension. Earlier studies [3, 4] have shown that a wide range of herbicides, pesticides, fungicides and insecticides can be completely photomineralized in the presence of TiO$_2$ and oxygen.

Bentazon (1) is a selective post-emergence herbicide, acting as a photosynthetic electron transfer inhibitor, used to control many broadleaf weeds and sedges primarily by contact action in most graminous and many large seeded leguminous crops [5]. Bentazon has the potential to contaminate both ground and surface water because of its low soil sorption and high water solubility. It is stable to hydrolysis and has a half life of less than 24 hours in water because it is readily broken down by sunlight [6]. Bentazon is slightly toxic by ingestion and by dermal absorption. Ingestion of higher doses in humans may cause vomiting, diarrhea, trembling, weakness and irritation to the skin, eyes, and respiratory tract [7, 8].

The pesticide compounds, Chloramben (2) and Cyanazine (3) are used as a pre- and post emergence herbicide for the control of annual grasses and broadleaf weeds in corn, sorghum, cotton, potato, soyabean etc.[9]. Chloramben was found to be persistent contaminant in Ontario wells supposed to find its way through leaching
The pesticide compound Cyanazine has been found in the ground water of two U.S. states (Iowa and Pennsylvania) at concentrations ranging between 0.1-1.0 µg/L. The general population is exposed to these herbicides from contaminated drinking water or food. Few studies related to photodegradation of Bentazon [13-15], Chloramben [16-18] and Cyanazine [19-21] have been reported earlier by different groups of workers but no major efforts have been made to study the detailed degradation kinetics and photocatalytic transformations of these pesticide compounds. Therefore, we have studied the detailed degradation kinetics of the pesticide compounds 1-3, shown in Chart 3.1, in aqueous suspensions of TiO₂ under different conditions and also identified the intermediate products formed during the photoxidation process using GC-MS analysis technique.

3.3 Experimental

3.3.1. Reagents and chemicals

All three pesticide derivatives 1-3 were purchased from Sigma- Aldrich India and were used without further purification. Heterogeneous photocatalytic tests were carried out using Degussa P25 TiO₂ (Degussa AG, anatase: rutile: 80:20, specific BET 50 m²g⁻¹, particle size 21 nm) [22]. Other TiO₂ catalyst powders used for comparison are Hombikat UV100 (Sachtleben Chemie GmbH, anatase, specific BET 250 m²g⁻¹, particle size 5-10 nm) and PC500 (Millennium Inorganic Chemicals, anatase, specific BET 320 m²g⁻¹, particle size 5-10 nm) [23, 24]. All other chemicals used in this study such as sodium hydroxide, nitric acid, hydrogen peroxide (30%), was of reagent grade and obtained from Merck. Double distilled water was used throughout the work.
Bentazon (1)

3-Isopropyl-1H - 2,1,3-benzothiadiazin-4,(3H) -one 2,2-dioxide (C$_{10}$H$_{12}$N$_{2}$O$_{3}$S)

Chloramben (2)

3-amino-2, 5-dichlorobenzoic acid (H$_2$NC$_6$H$_2$(Cl)$_2$CO$_2$H)

Cyanazine (3)

2-(4-chloro-6-(ethylamino)-1,3,5-triazin-2-ylamino)-2-methylpropanenitrile (C$_9$H$_{13}$ClN$_6$)

Chart 3.1: Chemical structure, Common name, IUPAC name and Empirical formula of pesticides 1-3.
3.3.2. Procedures

Experiments were carried out in an immersion well photoreactor made of Pyrex glass equipped with a magnetic bar, a water circulating jacket and an opening for molecular oxygen. Required amount of the photocatalyst was then added and equilibration of the solution was assured by continuous stirring and atmospheric oxygen supply for at least 15 minutes in the dark. Irradiations were carried out using 125 W medium pressure mercury lamps (Philips). The light intensity, as measured by UV-light intensity detector (Lutron UV-340), was found to be in the range of 1.49-1.88 mW/cm².

For the photocatalytic experiments, 250 mL of the pesticide solution containing the appropriate quantity of the semiconductor powder was taken in an immersion well photochemical reactor and stirred magnetically, while the solution was purged continuously with atmospheric oxygen. At specific time intervals samples of 6 mL were withdrawn, centrifuged in order to remove TiO₂ and subsequently analyzed. The reaction temperature was kept constant at 20±0.3 °C using refrigerated circulating water bath. Some photocatalytic experiments were repeated three times in order to check the reproducibility of the experimental results. The accuracy of the optical density and TOC values were within ±5%. The pH of the reaction mixture was adjusted by adding dilute aqueous solution of NaOH (1 mM) or HNO₃ (1 mM).

3.3.3. Analytical methods

The photocatalyzed degradation (decrease in pesticide concentration) of pesticide derivatives 1-3 was followed by measuring the change in absorbance at their $\lambda_{\text{max}}$ 225, 299 and 238 nm respectively using UV-Vis spectrophotometer (Shimadzu UV-1601) whereas the mineralization (Depletion in TOC vs. Irradiation time) was monitored by measuring the Total Organic Carbon (TOC) content with a Shimadzu
TOC\textsubscript{VCSH} Analyzer by directly injecting the aqueous solutions of irradiated samples. The concentration of the compounds was calculated by calibration curves obtained from the absorbance measurement at different known concentrations. For each experiment, the mineralization rate of the pesticide derivatives was calculated from the slope obtained by linear regression of the plot of natural logarithm of TOC as a function of irradiation time.

For the intermediate analysis, aqueous solution of the pesticide of desired concentration was irradiated for higher time intervals and the catalyst was removed through filtration. The filtrate was extracted with chloroform, subsequently dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure to give the residual mass which was analyzed by GC-MS. For GC-MS analysis, AccuTOF GCv (JMS-T100GCv) system from Jeol Asia equipped with Agilent 7690 GC was used. The GC column for separation was a HP-5, 30 m long and 0.25 mm internal diameter. The film thickness was 0.25 microns. The column temperature programme initially used was 100 °C with an isothermal hold time for 5 minutes and then rose to 280 °C at a ramp of 10 °C/min. The injector temperature was 250 °C and the injection volume was 0.4 µL, with a split ratio 1:50. The interface temperature was maintained at 280 °C. The carrier gas was helium with a flow rate 1 mL/min.

3.4 Results and discussion

3.4.1 Photolysis of aqueous suspensions of pesticide derivative 1 in the presence and absence of TiO\textsubscript{2}

Irradiation of an aqueous suspension of pesticide derivative 1 in the presence of TiO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} with constant bubbling of atmospheric oxygen lead to decrease in pesticide concentration and depletion in TOC content as a function of time. Figure 3.1 (a) shows the decrease in absorption intensity at its $\lambda_{\text{max}}$ (225 nm) as a function of
irradiation time in the presence of TiO$_2$ and H$_2$O$_2$. Figure 3.1 (b) depicts the change in concentration and depletion in TOC content as a function of irradiation time of an aqueous suspension of 1 in the presence and absence of TiO$_2$. It is obvious from the figure that the irradiation of 1 in the presence of H$_2$O$_2$ and UV light without TiO$_2$ lead to 9% mineralization and 9.5% degradation after 90 minutes. The corresponding values increased to 59.7% and 92.7% respectively when Bentazon was irradiated for the same time period in the presence of TiO$_2$.

3.4.2 Photolysis of aqueous suspensions of pesticide derivative 2 in the presence and absence of TiO$_2$

An aqueous suspension of pesticide derivative 2 was irradiated in the presence of TiO$_2$ and H$_2$O$_2$ under analogous conditions. Figure 3.2 (a) shows the decrease in absorption intensity at its $\lambda_{\text{max}}$ (299 nm) whereas the Figure 3.2 (b) depicts the change in concentration and depletion in TOC content as a function of irradiation time in the presence and absence of photocatalyst. It could be seen from the figure that in the presence of H$_2$O$_2$ and UV light, only 12.5% mineralization of Chloramben was observed after 90 minutes of irradiation whereas 15.5% degradation was observed after 45 minutes of irradiation. The corresponding values increased to 97.4% and 98.5% respectively when Chloramben was irradiated in the presence of both TiO$_2$ and H$_2$O$_2$ for the same time period.

3.4.3 Photolysis of aqueous suspensions of pesticide derivative 3 in the presence and absence of TiO$_2$

Irradiation of an aqueous suspension of pesticide derivative 3 in the presence of TiO$_2$ and H$_2$O$_2$ under similar conditions leads to decrease in pesticide concentration and depletion in TOC content as a function of irradiation time.
Figure 3.1 (a): Change in absorption intensity of Bentazon at its $\lambda_{\text{max}}$ 225 nm at different time interval on irradiation of an aqueous suspension of Bentazon in the presence of TiO$_2$ under constant stirring and bubbling of atmospheric oxygen. (b): Change in concentration and TOC content as a function of irradiation time of an aqueous suspension of Bentazon in the presence and absence of photocatalyst.

**Experimental conditions:** Immersion well photoreactor made up of Pyrex glass, Light source: 125W medium pressure Hg lamp, [Bentazon] = 0.5 mM, [H$_2$O$_2$] = 30 mM, Photocatalysts TiO$_2$: [P25] = 1 gL$^{-1}$, Vol. = 250 mL, Light intensity (1.86 – 1.88 mW/cm$^2$). Irradiation Time = 90 min.
Figure 3.2 (a): Change in absorption intensity of Chloramben (2) at its $\lambda_{\text{max}}$ 299 nm at different time interval on irradiation of an aqueous suspension of Bentazon in the presence of TiO$_2$ under constant stirring and bubbling of atmospheric oxygen. Absorbance was followed at 299 nm after 25% dilution. (b) Change in concentration and TOC content as a function of irradiation time of an aqueous suspension of Chloramben in the presence and absence of photocatalyst.

**Experimental conditions:** Immersion well photoreactor made up of Pyrex glass, Light source: 125W medium pressure Hg lamp, [Chloramben] = 1.0 mM, [H$_2$O$_2$] = 30 mM, Photocatalysts TiO$_2$: [P25] = 1 gL$^{-1}$, Vol. = 250 mL, Light intensity (1.86 – 1.88 mW/cm$^2$). Irradiation Time = 45 min. (UV analysis) and 90 min (TOC analysis).
Figure 3.3 (a) shows the decrease in absorption intensity at its $\lambda_{\text{max}}$ (238 nm) as a function of irradiation time in the presence of TiO$_2$ and H$_2$O$_2$. Figure 3.3 (b) depicts the change in concentration and depletion in TOC content as a function of irradiation time of an aqueous suspension of 3 in the presence and absence of TiO$_2$. As shown in Figure 3.3 (b), in the presence of H$_2$O$_2$ and photocatalyst, 89.9 % mineralization of Cyanazine was observed after 90 minutes whereas 90.4 % degradation was observed after 60 minutes of irradiation. On the other hand, in the absence of photocatalyst only 1.3 % mineralization and 1.6 % degradation was observed.

The curves for the depletion of TOC Vs irradiation time (mineralization) and decrease in concentration Vs irradiation time (degradation) for pesticide derivatives 1-3, can be fitted reasonably well by an exponential decay curve suggesting pseudo-first order kinetics. For each experiment, the rate constant for the mineralization or degradation was calculated from the plot of the natural logarithm of the TOC content or concentration of the herbicide as a function of irradiation time. The rate of mineralization and degradation for the herbicides were calculated in term of molL$^{-1}$min$^{-1}$ using formula given below:

$$\frac{-d[\text{TOC}]}{dt} = kC^n$$ (1)

$$\frac{-d[C]}{dt} = kC^n$$ (2)

$TOC =$ Total Organic Carbon, $C =$ concentration of the pollutant, $k =$ rate constant, $n =$ order of reaction.
Figure 3.3 (a) Change in absorption intensity of Cyanazine (3) at its \( \lambda_{\text{max}} \) 238 nm at different time interval on irradiation of an aqueous suspension of Cyanazine in the presence of TiO\(_2\) under constant stirring and bubbling of atmospheric oxygen. Absorbance was followed at 238 nm after 25% dilution. (b) Change in concentration and TOC content as a function of irradiation time of an aqueous suspension of Cyanazine in the presence and absence of photocatalyst.

**Experimental conditions:** Immersion well photoreactor made up of Pyrex glass, Light source: 125W medium pressure Hg lamp, [Cyanazine] = 0.5 mM, [\( \text{H}_2\text{O}_2 \)] = 20 mM, Photocatalyst TiO\(_2\): [P25] = 1 gL\(^{-1}\), Vol. = 250 mL, Light intensity (1.86 – 1.88 mW/cm\(^2\)). Irradiation Time = 60 min. (UV analysis) and 90 min (TOC analysis).
3.4.4. Effect of different TiO₂ Photocatalysts on the degradation and mineralization of pesticide derivatives 1-3

The photocatalytic degradation and mineralization of pesticide derivatives 1-3 was tested with three different commercially available TiO₂ powders (namely Degussa P25, Hombikat UV100 and Millennium Inorganic PC500) in the presence and absence of H₂O₂. The degradation of all three compounds 1-3 were found to proceed faster in the presence of H₂O₂ as compared with the experiments carried out in the absence of H₂O₂. The degradation and mineralization rate of 1-3 in the presence of three different TiO₂ samples with and without H₂O₂ is shown in Figure 3.4-3.6 respectively. In all three compounds the photocatalyst Degussa P25 was found to be better for degradation and mineralization as compared to other TiO₂ samples. Since the rates were found to be very slow in absence of H₂O₂, all following experiments were carried out in the presence of H₂O₂ in order to determine the detailed degradation kinetics under different conditions.

For better photocatalytic activity, the catalysts having smaller particle size with large surface area would result in better adsorption of compounds followed by interaction of light. According to particle size, BET surface area and percentage of anatase, the photocatalytic activity should be in the order of Hombikat UV100>PC500>Degussa P25 but this was not observed in this case. The actual order of activity observed in the case of pesticide derivatives 1-3 was Degussa P25>UV100>PC500 and is in accordance with the results obtained for the photocatalytic degradation of large number of organic pollutants [25-27]. The better photocatalytic activity of Degussa P25 could be attributed on the basis of the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile “catches” photons, generating electron- hole pairs.
Figure 3.4: Comparison of mineralization rate of Bentazon (1) in the presence of different photocatalysts.

**Experimental conditions:** Immersion well photoreactor made up of Pyrex, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Bentazon] = 0.5 mM, [H₂O₂] = 30 mM, [P25] = [UV100] = [PC500] = 1 gL⁻¹, Vol. = 250 mL, Irradiation Time = 90 min.
Figure 3.5: Comparison of degradation and mineralization rate of Chloramben (2) in the presence of different photocatalysts.

**Experimental conditions:** Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Chloramben] = 1.0 mM, [H₂O₂] = 30 mM, [P25] = [UV100] = [PC500] = 1 gL⁻¹, Vol. = 250 mL, Irradiation Time = 45 min (UV analysis) and 90 min (TOC analysis).
Figure 3.6 Comparison of degradation and mineralization rate of Cyanazine (3) in the presence of different photocatalysts.

Experimental conditions: Reaction vessel: immersion well photoreactor made up of Pyrex glass, light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Cyanazine] = 0.5 mM, [H₂O₂] = 20 mM, [P25] = [UV100] = [PC500] = 1 gL⁻¹, Vol. = 250 mL, Irradiation Time = 60 min (UV analysis) and 90 min (TOC analysis).
The electron transfer from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react [28]. In one of the earlier study [29] the better photocatalytic activity of Degussa P25 has been shown to be on the basis of the fact that P25 owes its high photo-reactivity due to slow recombination between electron and holes whereas Sachtleben Hombikat UV100 has a high photo reactivity due to fast interfacial electron transfer rate. Since the photocatalyst Degussa P25 was found to be more active photocatalyst, it is obvious that the rate-limiting step cannot be interfacial electron transfer rate but rather lifetime of electron hole pairs.

3.4.5. Effect of catalyst dosage on the degradation and mineralization of pesticide derivatives 1-3

For economic removal of pollutants from the waste water using heterogeneous photocatalysis, the optimum amount of catalyst is necessary to be determined for efficient degradation since reaction rate has been found to be dependent on the catalyst loadings [30-33].

The photocatalytic degradation and mineralization of pesticide derivatives 1-3 in the presence of H₂O₂ at different TiO₂ concentrations (P25 and UV100) has been investigated and the results are depicted in Figure 3.7-3.9 respectively. The photocatalytic rate of degradation and mineralization of three compounds was found to increase initially with increase in catalyst loading from 0.5 to 1gL⁻¹ and a further increase in catalyst dosage lead to decrease in degradation rate. This may be due to the fact that at high catalyst loading light scattering and screening effects reduces the photonic flux within the irradiated solution. Moreover at higher catalyst concentration, the tendency towards agglomeration increases and the increased turbidity of the suspension reduces the light transmission [34].
Figure 3.7: Effect of catalyst concentration on mineralization rate of Bentazone (1).

**Experimental conditions:** Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Bentazon] = 0.5 mM, [H₂O₂] = 30 mM, [P25] = [UV100] = 1 gL⁻¹, Vol. = 250 mL, Irradiation Time = 90 min.
Figure 3.8: Effect of catalyst concentration degradation and mineralization rate of Chloramben (2).

Experimental conditions: Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Chloramben] = 1.0 mM, [H₂O₂] = 30 mM, [P25] = [UV100] = 1 gL⁻¹, Vol. = 250 mL, Irradiation Time = 45 min (UV analysis) and 90 min (TOC analysis).
Figure 3.9: Effect of catalyst concentration on degradation and mineralization rate of Cyanazine (3) in the presence of different photocatalysts.

Experimental conditions: Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Cyanazine] = 0.5 mM, [H₂O₂] = 20 mM, [P25] = [UV100] = 1 gL⁻¹, Vol. = 250 mL, Irradiation Time = 60 min (UV analysis) and 90 min (TOC analysis).
It is important to mention here that this optimum amount of catalyst depends on the initial concentration of the pollutant, geometry and the working conditions of the reactor and corresponds to the optimum of light absorption [35]. The optimum amount of $1\text{gL}^{-1}$ TiO$_2$ has been suggested for the photocatalytic degradation of various herbicides [34, 36].

3.4.6. Effect of Initial pH on the degradation and mineralization of pesticide derivatives 1-3

The surface properties of metal oxides under acidic or alkaline conditions can have considerable implications upon their photocatalytic activity [37], therefore solution pH is an important parameter that influences the photocatalytic degradation and mineralization of organic pollutants. Employing Degussa P25 as photocatalyst the rate of mineralization for pesticide compounds 1-3 in the presence of hydrogen peroxide was studied in the pH range 1-10. In case of Bentazon (1) the photocatalytic mineralization rate was found to increase with the increase in initial pH from 2.0 to 5.2 and then decreased with further increase in pH as shown in Figure 3.10. In case of Chloramben (2), the rate was found to increase with increase in pH from 1.2 to 6.8 and then decreased with any further increase in pH as shown in Figure 3.11. In case of Cyanazine (3), highest rate was observed at pH 2.2 which was found to decrease slowly with increase in pH as shown in Figure 3.12.

Since the pH$_{pzc}$ of TiO$_2$ is about 6.25 [38], the TiO$_2$ surface will be positively charged (Eq. (3)) in acidic medium (pH<6.25) whereas it will be negatively charged (Eq. (4)) in alkaline medium (pH>6.25).

\[
\text{When pH<Pzc: } \text{TiOH} + \text{H}^+ \leftrightarrow \text{TiOH}_2^+ \quad (3)
\]

\[
\text{When pH>Pzc: } \text{TiOH} + \text{OH}^- \leftrightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (4)
\]
Figure 3.10: Effect of initial pH on the mineralization rate of Bentazon (1).

Experimental conditions: Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Bentazon] = 0.5 mM, [H₂O₂] = 30 mM, [P25] = 1 gL⁻¹, [Initial pH] = 2.2, 3.3, 5.2, 6.3, 7.9 and 9.3, Vol. = 250 mL, Irradiation Time = 90 min.
Figure 3.11: Effect of initial pH on the degradation and mineralization rate of Chloramben (2).

**Experimental conditions:** Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Chloramben] = 1.0 mM, [H₂O₂] = 30 mM, [P25] = 1 gL⁻¹, [Initial pH] = 1.2, 3.2, 6.8 and 9.5, Vol. = 250 mL, Irradiation Time = 45 min (UV analysis) and 90 min (TOC analysis).
Figure 3.12: Effect of initial pH on the degradation and mineralization rate of Cyanazine (3).

Experimental conditions: Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm²), [Cyanazine] = 0.5 mM, [H₂O₂] = 20 mM, [P25] = 1 gL⁻¹, [Initial pH] = 2.2, 4.4, 6.3 and 8.6, Vol. = 250 mL, Irradiation Time = 60 min (UV analysis) and 90 min (TOC analysis).
The $pK_a$ of Bentazon (1) has been reported to be 3.3 [39]. The increase in mineralization rate with increase in pH from 2.2 to 5.2 may be attributed to the efficient adsorption of substrate on catalyst surface due to attraction between positively charged TiO$_2$ surface and negatively charged Bentazon molecules. Further increase in pH decreases the mineralization rate since repulsive forces between negatively charged catalyst surface and negatively charged Bentazon molecules decreases the adsorption and hence the photocatalytic process. The $pK_a$ value of Chloramben (2) has been reported as 3.4 [40]. The better rate at neutral pH could be attributed to zwitterionic form of Chloramben leading to better adsorption on the surface of the photocatalyst. The lower rate at acidic and alkaline pH could be due to electrostatic repulsion between ionic Chloramben and charged TiO$_2$ particles.

The $pK_a$ value of Cyanazine (3) has been reported as 0.63 [41]. The better degradation rate of Cyanazine in acidic pH may be attributed on the basis of the fact that the compound will be fully in the anionic form within the pH range studied. At lower pH values, adsorption will occur due to anionic form of compound 3 and the positively charged TiO$_2$ resulting in better degradation rate. With the increase in pH the negatively charged titanium dioxide surface would repel the compound 3, and this repulsion would increase with increasing pH, resulting in a decrease in the photodegradation efficiency.

### 3.4.7. Effect of Hydrogen Peroxide Concentration on the degradation and mineralization of pesticide derivatives 1-3

The degradation and mineralization of pesticide derivatives 1-3 has been investigated in the presence of different H$_2$O$_2$ concentration in order to obtain the optimum value. The effect of different concentrations of hydrogen peroxide on the degradation and mineralization rate of pesticide derivatives 1-3 is respectively shown in
Figure 3.13-3.15. The rate was found to increase with the increase in hydrogen peroxide concentration from 10 mM to 30 mM in all three pesticide derivatives. Any further increase in hydrogen peroxide concentration had a negative effect on the rate of degradation and mineralization. The increase in reaction rate by H$_2$O$_2$ addition could be attributed to its better electron acceptance power (Eq. 5) thereby reducing electron hole recombination as well as increase in the number of hydroxyl radicals produced which are required for the degradation of organic pollutants [42]. The hydroxyl radicals can also be formed by interaction of hydrogen peroxide with superoxide radicals (Eq. 6). Above optimum value the competitive reactions between hydroxyl radical and peroxide lead to the generation of less reactive hydroperoxide radical which does not contribute to the degradation of organic substrate (Eq. 7) [43]. The inhibition of degradation rate can also be explained in terms of TiO$_2$ surface modification by H$_2$O$_2$ adsorption resulting in scavenging of photo produced holes [44] (Eq. 8).

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{e}^-_{\text{CB}} & \rightarrow \cdot \text{OH} + \text{OH}^\cdot \quad (5) \\
\text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow \cdot \text{OH} + \text{OH}^\cdot + \text{O}_2 \quad (6) \\
\text{H}_2\text{O}_2 + \cdot \text{OH} & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (7) \\
\text{H}_2\text{O}_2 + 2\text{h}^+ & \rightarrow \text{O}_2 + 2\text{H}^+ \quad (8)
\end{align*}
\]
Figure 3.13: Effect of H$_2$O$_2$ concentration on mineralization rate of Bentazon (1).

**Experimental conditions:** Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm$^2$), [Bentazon] = 0.5 mM, [H$_2$O$_2$] = 10, 20, 30 and 40 mM, [P25] = [UV100] = 1 gL$^{-1}$, Vol. = 250 mL, Irradiation Time = 90 min.
Figure 3.14: Effect of H$_2$O$_2$ concentration on the degradation and mineralization rate of Chloramben (2).

Experimental conditions: Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm$^2$), [Chloramben] = 1.0 mM, [H$_2$O$_2$] = 10, 20, 30 and 40 mM, [P25] = 1 gL$^{-1}$, Vol. = 250 mL, Irradiation Time = 45 min (UV analysis) and 90 min (TOC analysis).
Figure 3.15: Effect of H$_2$O$_2$ concentration on the degradation and mineralization rate of Cyanazine (3).

**Experimental conditions:** Reaction vessel: immersion well photoreactor made up of Pyrex glass, Light source: 125 W medium pressure mercury lamp, Light intensity (1.86 – 1.88 mW/cm$^2$), [Cyanazine] = 0.5 mM, [H$_2$O$_2$] = 10, 20, 30 and 40 mM, [P25] = 1 gL$^{-1}$, Vol. = 250 mL, Irradiation Time = 60 min (UV analysis) and 90 min (TOC analysis).
3.5. Intermediate product analysis

3.5.1. Photocatalytic transformation of Bentazon (1)

An attempt was made to identify the intermediate products formed during the photocatalytic degradation of Bentazon (1) in the presence of titanium dioxide using GC-MS analysis technique. An aqueous solution of Bentazon (1.85 mM, 180 mL) was irradiated with 125W medium pressure mercury lamp in the presence of TiO$_2$ (Degussa P25 1.5gL$^{-1}$) under constant stirring and bubbling of atmospheric oxygen for different time intervals. GC analysis of unirradiated and irradiated samples (6 hr) of Bentazon is shown in Figure 3.16 (a & b).

Analysis of unirradiated sample indicates a single peak at retention time (R$_t$) 12.9 corresponding to Bentazon as confirmed by NIST library whose molecular ion and mass fragmentation pattern is shown in Table 3.1. Analyses of the irradiated mixture of 1 for six hours indicate the formation of several products as shown in Figure 3.16 (b). The structure of photoproducts has been proposed on the basis of molecular ion, mass fragmentation pattern and also on comparison with the NIST library. It is interesting to note that none of the hydroxyl derivatives of Bentazon were observed in our case as has been reported to be formed during its degradation in soil, photolytic and photocatalytic conditions in several earlier studies [14, 45, 46].

The structure of the product 2 (m/z 178) has been confirmed by comparing its molecular ion and mass fragmentation pattern with NIST library. The mass fragmentation of the product 9 (m/z 193) is shown in Scheme 3.1. Loss of methyl radical gives radical cation at m/z 178. The most abundant peak at m/z 150 corresponds to the loss of isopropyl radical. Subsequent loss of nitrosyl radical gives cation at m/z 120 which upon further loss of carbonyl group gives cation at m/z 92. Alternatively the cation at m/z 150 may lose $^{1}$NH$_2$ radical to give radical cation...
Figure 3.16: Gas Chromatogram of Bentazon (1); (a) Unirradiated Bentazon, (b) Irradiated sample (6 hr).
Table 3.1: Probable products formed during the photocatalytic degradation of Bentazon (1) along with their retention time and corresponding mass fragmentation.

<table>
<thead>
<tr>
<th>Retention time</th>
<th>Name</th>
<th>Confirmed by</th>
<th>Mass Fragmentation Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.9</td>
<td>3-Isopropyl-1H -2,1,3-benzothiadiazin-4,(3H) -one 2,2-dioxide, Bentazone (1)</td>
<td>NIST</td>
<td>240(M⁺), 225, 198, 182, 161, 119, 92 and 64</td>
</tr>
<tr>
<td>12.5</td>
<td>N-isopropyl-2-nitrobenzamide (8)</td>
<td>Mass fragmentation</td>
<td>208(M⁺), 180, 152, 139, 125, 111, 97, 83, 69 and 56</td>
</tr>
<tr>
<td>12.3</td>
<td>N-isopropyl-2-nitrosobenzamide (9)</td>
<td>Mass fragmentation</td>
<td>193(M⁺), 178, 150, 134, 120, 104, 92, 76 and 58</td>
</tr>
<tr>
<td>8.8</td>
<td>2-amino-N-isopropylbenzamide (5)</td>
<td>NIST</td>
<td>178(M⁺), 120, 92,65 and 58</td>
</tr>
<tr>
<td>7.0</td>
<td>N-isopropylbenzamide (7)</td>
<td>Mass fragmentation</td>
<td>163(M⁺), 135, 106, 93, 86, 70 and 56</td>
</tr>
<tr>
<td>4.3</td>
<td>2-aminobenzoic acid (4)</td>
<td>Mass fragmentation</td>
<td>138(M⁺), 106, 59, 44</td>
</tr>
</tbody>
</table>

Note: Number in the parenthesis corresponds to the number of the compound in the degradation scheme.
at m/z 134 which upon further loss of nitrosyl radical gives radical cation at m/z 104. Similarly the mass fragmentation pathway of the product 8 (m/z 208) is shown in Scheme 3.2.

The molecular ion and mass fragmentation pathway of the product 7 (m/z 163) is given in Scheme 3.3. The most abundant peak at m/z 135 corresponds to the loss of carbonyl group. Further loss of propene leads to the formation of aniline radical cation (m/z 93). The peak at m/z 106 corresponds to benzaldehyde radical cation formed via α-cleavage of precursor ion at m/z 163. Alternatively loss of phenyl radical leads to the formation of oxonium cation at m/z 86 which upon further loss of methane molecule leads to another oxonium cation at m/z 70. On the basis of the above results and assumptions, a probable degradation pathway of Bentazon (1), in aqueous suspension of TiO₂ under exposure to UV light, was proposed as described in Scheme 3.4. It should be mentioned here that products 4, 5, 8 and 9 have been reported to be formed during the direct photolytic exposure of Bentazon [47]. Moreover, products 4 and 5 have also been reported as degradation metabolites of Bentazon in soil. Thus the initial loss of SO₂ gives product 5. Addition of hydroxyl radical and subsequent loss of isopropyl amine leads to 2-aminobenzoic acid (4). The oxidation of NH₂ group of product 5 leads to nitrosyl derivative 9 via intermediate 6. Further oxidation of product 9 gives nitro derivative 8. The conversion of NH₂ to NO₂ via NO during photocatalytic treatments in the presence of TiO₂ is well documented in literature [48-51].
Scheme 3.1: Proposed Fragmentation pathways for the ion [9+H]^+ of m/z 193.

Scheme 3.2: Proposed Fragmentation pathways for the degradation product 8 of m/z 208.
**Scheme 3.3:** Proposed Fragmentation pathways for the degradation product 7 of m/z 163.

**Scheme 3.4:** Possible route for the photocatalytic degradation of Bentazon (1) in the presence of TiO₂ via the formation of products 4-9.
3.5.2. Photocatalytic transformation of Chloramben (2)

GC analysis of an unirradiated (0 h) and irradiated mixture (6 and 10 h) of Chloramben (2) in acetonitrile water mixture in the presence of TiO₂ with constant bubbling of air is shown in Figure 3.17 (a-c). Analysis of the unirradiated sample indicate a single peak at retention time (Rₜ) 11.3 min corresponding to the Chloramben as confirmed by NIST library whose molecular and mass fragmentation pattern is shown in Table 3.2. Analysis of the irradiated mixture of 2 for six and ten hours indicates the formation of several products as shown in Table 3.2. The structures of photoproducts have been proposed on the basis of molecular ion, mass fragmentation pattern and also on comparison with the NIST library. The formation of different products during the photocatalytic degradation of Chloramben can be understood in terms of the pathway shown in Scheme 3.5. The major route for the formation of various products from 2 involves the dechlorination and deamination reactions. The model compound 2 upon the transfer of an electron can form the radical anion 10 which may either lose Cl⁻ to give 11 or NH₃ molecule to give 12. Both 11 and 12 after further transfer of electrons can lead to the formation of product 13 which may again lose another Cl⁻ to give the observed product 14. The structures of the products 11-14 were identified by comparing their mass fragmentation with the NIST library.
Figure 3.17: Gas Chromatogram of Chloramben (2); (a) Unirradiated Chloramben, (b) Irradiated sample (6 hr), (c) Irradiated sample (10 hr).
Table 3.2: Probable products formed during the photocatalytic degradation of Chloramben (2) along with their retention time and corresponding mass fragmentation.

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Name</th>
<th>Confirmed by</th>
<th>Mass fragmentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4</td>
<td>3-amino-2,5-dichlorobenzoic acid Chloramben (2)</td>
<td>NIST</td>
<td>209.03 (M+) / 206.98 / 205, 188, 162, 124.02 and 62.03</td>
</tr>
<tr>
<td>9.7</td>
<td>3-amino-5-chlorobenzoic acid (11)</td>
<td>NIST</td>
<td>171 (M+) / 173, 154 / 156, 126 / 128, 90, 63 and 52</td>
</tr>
<tr>
<td>7.9</td>
<td>2,5-dichlorobenzoic acid (12)</td>
<td>NIST</td>
<td>189.99 (M+) / 191.99 / 194.04, 172.98 / 174.99, 156.03, 144.99, 139.02, 111.02 and 75.03</td>
</tr>
<tr>
<td>5.4</td>
<td>Chlorobenzoic acid (13)</td>
<td>NIST</td>
<td>158.02 (M+) / 156.01, 139.01 / 141.01, 111.01 / 113.01, 75.03 and 50.02</td>
</tr>
<tr>
<td>3.5</td>
<td>Benzoic acid (14)</td>
<td>NIST</td>
<td>122.05 (M+), 105.04 / 106.06, 77.04 and 51.03</td>
</tr>
</tbody>
</table>

Note: Number in the parenthesis corresponds to the number of the compound in the degradation scheme.
Scheme 3.5: Proposed photocatalytic degradation pathway of Chloramben (2) in presence of TiO$_2$. 

![Diagram of the photocatalytic degradation pathway of Chloramben (2)]
3.5.3. Photocatalytic transformation of Cyanazine (3)

GC analysis of an unirradiated (0 h) and irradiated mixture (6 and 10 h) of Cyanazine (3) in acetonitrile water mixture in the presence of TiO2 with constant bubbling of air is shown in Figure 18 (a-b). Analysis of the mixture of 3 after six hours of irradiation indicated the formation of several products. The molecular ion and mass fragmentation data of Cyanazine and its various products are given in Table 3.3. Probable structures of photoproducts have been proposed on the basis of molecular ion and also by comparing the mass fragmentation with the NIST library. The major routes for degradation of Cyanazine are dealkylation, dechlorination, decyanation and hydroxylation reactions shown in Scheme 3.6. In case of Cyanazine, the structure of the products 16 and 18 has been confirmed by comparing their mass fragmentation with NIST library. It is interesting to note that the mass fragmentation pattern obtained here for products 16 (m/z 201) and 18 (m/z 173) is similar to those proposed by Jörg et. al [52] and Ross & Tweedy [53]. According to the above authors the most common fragmentation pathway for the molecular ions of chlorinated s-triazines containing alkyl amino side chains is α-cleavage and McLafferty rearrangements. The structure of the products 15 (m/z 223) and 19 (m/z 212) have been proposed on the basis of mass fragmentation pattern shown in Scheme 3.7 and 3.8 respectively. The protonated molecular ion of 15 (m/z 223) indicates the absence of chlorine atom whereas its molecular mass prior to protonation m/z 222 indicates a molecule containing an even number of nitrogen atoms. The most abundant ion at m/z 195 corresponds to the elimination of ethene (loss of 28) from ethyl amino side chain. Subsequent loss of CO molecule gives rise to the cation at m/z 167 which after further
Figure 3.18: Gas Chromatogram of Cyanazine (3); (a) Unirradiated Cyanazine, (b) Irradiated sample (6 hr).
Table 3.3: Probable products formed during the photocatalytic degradation of Cyanazine (3) along with their retention time and corresponding mass fragmentation.

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Name</th>
<th>Confirmed by</th>
<th>Mass fragmentation pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.8</td>
<td>2-(4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-ylamino)-2-methylpropanenitrile (15)</td>
<td>Mass Fragmentation</td>
<td>223.14 (M+H), 208.12, 195.10, 180.11, 166.12, 152.11, 139.08, 137.08, 111.07, 97.07, 83.07 and 69.02</td>
</tr>
<tr>
<td>13.2</td>
<td>2-(4-chloro-6-(methylamino)-1,3,5-triazin-2-ylamino)-2-methylpropanenitrile (17)</td>
<td>Mass Fragmentation</td>
<td>225.10 (M⁺), 212.09 / 214.10, 184.07 / 185.08, 170.06, 161.09, 145.03 / 147.04, 129.02, 110.06, 104.02, 86.99, 83.07, 68.03 / 67.03 and 43.04</td>
</tr>
<tr>
<td>12.7</td>
<td>2-(4-chloro-6-(ethylamino)-1,3,5-triazin-2-ylamino)-2-methylpropanenitrile (3)</td>
<td>NIST</td>
<td>240.12 (M⁺) / 242.12, 227.09 / 225.10, 212.10, 198.08, 174.06 / 173.07, 158.08, 145.03, 138.09, 110.06, 96.06, 89.03, 55.03 and 44.05</td>
</tr>
<tr>
<td>12.0</td>
<td>2-(4-amino-6-chloro-1,3,5-triazin-2-ylamino)-2-methylpropanenitrile (19)</td>
<td>Mass Fragmentation</td>
<td>212.09 (M⁺), / 214.10, 184.06 / 185.07, 170.05, 161.09, 145.03 / 147.04, 129.01, 110.06, 83.07, 68.03 / 67.03 and 43.04</td>
</tr>
<tr>
<td>10.1</td>
<td>6-chloro-N²,N⁴-diethyl-1,3,5-triazine-2,4-diamine (16)</td>
<td>NIST</td>
<td>201.11 (M⁺) / 203.11, 200.11, 186.09, 173.08, 158.07, 154.13, 145.05, 139.11, 132.7, 126.10, 111.08, 96.07, 76.06, 71.07, 68.03, 55.07 and 43.04</td>
</tr>
<tr>
<td>9.0</td>
<td>6-chloro-N²-ethyl-1,3,5-triazine-2,4-diamine (18)</td>
<td>NIST</td>
<td>173.08(M⁺) / 175.08, 158 / 160.06, 154.12, 145.04, 139.10, 126.09, 111.08, 91.07, 85.07, 69.05 / 68.03, 55.05 and 43.04</td>
</tr>
</tbody>
</table>

Note: Number in the parenthesis corresponds to the number of the compound in the degradation scheme.
Scheme 3.6: Possible route for the photocatalytic transformation of Cyanazine (3) in the presence of TiO$_2$ via the formation of products 15-19.
Scheme 3.7: Proposed Fragmentation pathways for the degradation product 15 of m/z 223.
elimination of N\textsubscript{2} molecule (loss of 28) gives abundant ion at m/z 139. Loss of H\textsubscript{2} molecule leads to cation at m/z 137.

Expulsion of cyanide radical could then lead to the observed radical cation at m/z 111. The [M-15] radical cation at m/z 208 might arise by loss of methyl radical from side chain. Subsequent elimination of ethene from ethyl amino side chain together with hydrogen migration leads to the product ion at m/z 180 which after further loss of CO molecule gives product ion at m/z 152. The presence of product ion at m/z 97 formed via the rupture of the triazine ring is characteristic in the MS/MS spectra of ethylhydroxytriazines [54]. This ion after further loss of ethene via γ-hydrogen migration yields the ion at m/z 69. The presence of these ions (m/z 97 and 69) as well as absence of any M+2 peaks provide further evidence for the assignment of the molecular ion at m/z 223 belonging to the class of ethylhydroxytriazines. The presence of M+2 peaks in the mass spectra of product 19 (m/z 212) indicates the presence of chlorine atom. The most abundant ion at m/z 145 corresponds to the loss of methacrylonitrile (loss of 67) from the bulky side chain. The formation of the product ions at m/z 110, 68 and 43 from the precursor ion at m/z 145 has been explained by Ross & Tweedy [53]. The [M-28] ion at m/z 184 might arise by the loss of ethene from the alkyl amino side chain. Subsequent elimination of aminoacetonitrile radical (loss of 55) leads to the cation at m/z 129.
Scheme 3.8: Proposed Fragmentation pathways for the degradation product 19 of m/z 212.
References


