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Photocatalytic degradation of carbofuran using semiconductor oxides

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Abstract

The photocatalytic degradation of carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) was investigated in an aqueous solution using Degussa P-25 TiO_2 and ZnO as photocatalysts. The progress of degradation was monitored using TOC analyzer, HPLC, GC–MS and UV–vis spectrophotometer. The effects of various experimental parameters such as initial concentration of carbofuran, pH of the solution, catalyst loading and light intensity were systematically studied in order to achieve maximum degradation efficiency. The complete mineralization of carbofuran was confirmed by TOC analyzer. The degradation with ZnO showed less efficiency than TiO_2. The formation of NO_3^- was identified and quantified using HPLC. In addition, four different intermediates formed during the degradation process were also identified and characterized by GC–MS. The mineralization rate was compared with lamps of wavelength 254 and 365 nm under similar conditions. The rate with 254 nm was observed to be very close to that of 365 nm.
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1. Introduction

The presence of pesticides in the effluent of pesticide formulating and manufacturing industries severely affects the ecosystem. They are also used in different forms to overcome the loses from pests in the cultivation of plants. Though they contribute to a great extent in the agricultural productivity, they become major pollutants due to their extensive use. Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methyl carbamate), an insecticide and nameticide, is included in the general group of carbamate derivative pesticides. It is an active acetyl-cholinesterase inhibitor and is toxic to fish and mammals. Katsumata et al. [1] reported that more than five million pounds of carbofuran were applied in the United States in the year 1995. The use of carbofuran has received intensive concern not only due to its extensive use but also due to its high oral toxicity [2–4]. Due to its long persistence in water, it is increasingly detected in soil surface and wastewater. It exhibits refractory character to bio-degradation method [5]. Hence an effective and inexpensive technique is badly needed for treating such pollutant. Recently, it has been demonstrated that semi-conducting mate-

rials mediated photocatalytic oxidation of organic compounds is a successful, convenient alternative to conventional methods for the removal of organic pollutants from water. Among the various semiconducting materials, TiO_2 and ZnO are considered to be promising photocatalysts, particularly TiO_2 (anatase), due to its: (i) high photocatalytic activity, (ii) resistance to photocorrosion, and (iii) biological immunity. The high photocatalytic activity of anatase form of TiO_2 exhibits good application in the degradation of various organic pollutants [6–9]. The illumination of these semiconducting particles with light energy produces excited high-energy state of electron and hole pairs (e^-/h^+) that can migrate to the surface of the particle and initiate a wide range of redox reactions, which can lead to complete mineralization of organic pollutants. The degradation of these compounds takes place via formation of partially oxidized intermediates that also undergo degradation by fragmentation. The complete mineralization of carbofuran was achieved in 16 h with TiO_2 coated on glass plates [2]. Twenty percent Mineralization was observed with TiO_2 coated on the blades of agitator after 6 h [10]. In the present study TiO_2 was used as powder in batch reactor. The effects of experimental parameters such as concentration of carbofuran, pH of the solution, catalyst loading and light intensity on the degradation efficiency were examined and the results are discussed. The degradation efficiencies of TiO_2 and ZnO were also compared to select the suitable photocatalyst

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for the degradation of carbofuran. The degradation of carbofuran was also investigated with low-pressure mercury vapour lamps of wavelengths 254 and 365 nm and their efficiencies were compared. Furthermore, the photoproducts of carbofuran produced during the photocatalytic degradation process have been identified, and based on the formation of intermediates possible degradation pathway of carbofuran is proposed.

2. Experimental

2.1. Materials

The commercially available TiO_2 (Degussa P-25 having 70% anatase and 30% rutile, surface area $50\,m^2\,g^{-1}$ and particle size 25 nm) obtained from Degussa Chemical, Germany, was used as the photocatalyst without any further treatment. ZnO (Merck) having surface area $10\,m^2\,g^{-1}$ and particle size 0.1–4 μm was commercially procured and used as such. The technical grade sample of carbofuran was received from Sree Ramcides Chemicals, Chennai, India.

2.2. Procedures and analytical methods

Photocatalytic degradation of carbofuran was performed in an aqueous solution in a slurry batch reactor. The cylindrical photochemical reactor of 30 cm × 3 cm (height × diameter), provided with water circulation arrangement to maintain the temperature in the range 25–30 °C, was used in all the experiments. Irradiation was carried out using 8 W × 8 W low-pressure mercury lamps built into a lamp housing with polished anodized aluminium reflectors placed 12 cm away from the reactor. The lamps emitted predominantly UV radiation at a wavelength of 254 nm. The other eight lamps were arranged alternatively to emit UV radiation at a wavelength of 365 nm. The reactor set up was covered with aluminium foil followed by a black cloth to prevent UV light leakage. A stock solution containing $300\,mg\,l^{-1}$ of carbofuran was prepared in double distilled water and diluted to the required concentrations ($50–250\,mg\,l^{-1}$). TiO_2 (100 mg) was added to 100 ml of carbofuran solution ($200\,mg\,l^{-1}$) and the resultant slurry was stirred for 30 min to attain equilibrium adsorption. It was then irradiated with UV light of 254 nm with continuous purging of air free from CO_2. Aliquots were withdrawn at specific time intervals and analyzed after centrifugation followed by filtration with 0.2 μm membrane to remove titania particles. The change in the concentration of carbofuran was observed from its characteristic absorption band using a UV–vis spectrophotometer (Shimadzu-model 1601). Absorption peaks corresponding to carbofuran, which appeared at 210 and 275 nm, showed a linear dependence with initial concentration of carbofuran. The decrease in absorption maximum at 275 nm was observed with increasing reaction time in the degradation of carbofuran. The extent of degradation and formation of intermediates were followed using a high performance liquid chromatograph (HPLC) (Shimadzu, LC-10 ATvp pump and SPD-10Avp UV–vis detector adjusted to 210 nm, with reverse phase ODS column). The mobile phase was composed of acetonitrile and triple distilled

water (40:60, v/v), whose pH was adjusted to 3 using phosphoric acid. The extent of mineralization of carbofuran was followed with total organic carbon analyzer (Shimadzu TOC-V CPN). The degradation products, obtained during the photocatalytic degradation, were analyzed using GC–MS (Perkin-Elmer model Clarus 500). Under the optimized conditions, slurry containing 100 ml of $200\,mg\,l^{-1}$ carbofuran solution at pH 7 and 100 mg of TiO_2 powder was irradiated, centrifuged and filtered. This solution was immediately extracted with dichloromethane [3]. After separation from the aqueous solution, the organic phase was dried with anhydrous sodium sulphate. The GC–MS conditions were as follows: DP-1 (100% dimethylpolysiloxane) column, helium as carrier gas, initial temperature 80 °C, increment of 10 °C/min, injection port temperature 220 °C and detector temperature 250 °C. The formation of $NO_3{}^-$ ions was identified and confirmed by injecting the blank solution of sodium nitrate in HPLC. The peak at retention time of 1.76 min for the irradiated sample was found to coincide with the peak for sodium nitrate solution. The formation of $NH_4{}^+$ ions was confirmed with Nessler's reagent.

3. Results and discussion

The reaction variables such as: (i) pH of the solution, (ii) initial concentration of carbofuran, (iii) catalyst loading and (iv) light intensity on the rate of degradation were studied with light of 254 nm and the results are delineated below.

3.1. Effect of pH

The solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic reactions. The pH of the solution influences adsorption and dissociation of the substrate, catalyst surface charge, oxidation potential of the valence band and other physico-chemical properties of the system [11]. The effect of pH on the rate of photocatalytic degradation was studied by keeping all other experimental conditions constant and changing the initial pH value of the pesticide solution from 4 to 9, and the results are illustrated in Fig. 1. The rate of degradation
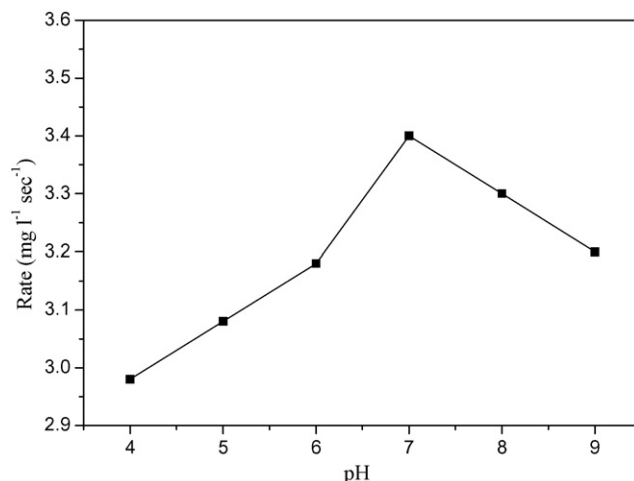

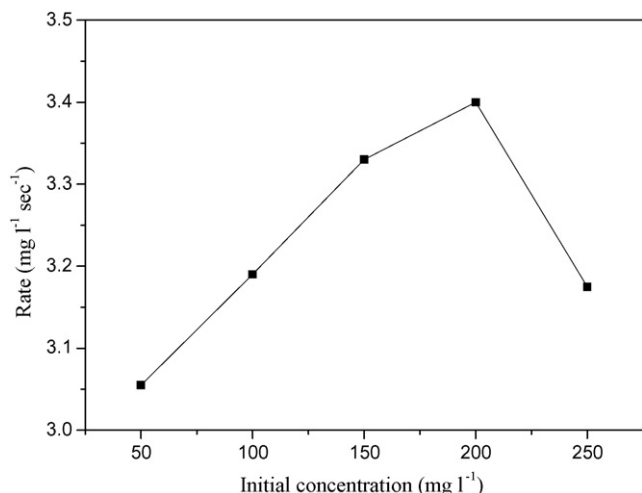
Fig. 1. Effect of solution pH on degradation rate.

Fig. 2. Effect of initial concentration on degradation rate.

Fig. 3. Effect of catalyst loading on degradation rate.

increases with increase in pH from 4 to 7 and then decreases. Since the pH_{zpc} of TiO_2 is 6.8, the surface of the catalyst is protonated and positive below pH 6.8. Again at such pH values carbofuran might also be protonated at the carbonyl oxygen. Such protonation might result in electrostatic repulsion between the catalyst and carbofuran and will reduce both adsorption and the rate of degradation. The decrease in degradation rate above pH 7 is due to negative charge of the carbofuran phenoxide ion by which it is repelled by the negative charge of the catalyst surface. It is also reported that hydrolysis of carbofuran produces carbofuran phenoxide in alkaline medium [12].

3.2. Effect of initial carbofuran concentration

The effect of initial concentration of carbofuran on the overall rate of degradation was studied by varying the initial concentration over a wide range from 50 to 250 mg l^{-1}. The results are illustrated in Fig. 2. The rate of degradation increases with increase in the carbofuran concentration up to 200 mg l^{-1}. The rate of degradation is related to the formation of $^\bullet$OH radicals, which is the critical species in the degradation process. But above this optimal concentration the rate decreases due to insufficient quantity of $^\bullet$OH radicals, as the formation of $^\bullet$OH radicals is constant for a given amount of the catalyst [11].

3.3. Effect of catalyst loading

The effect of catalyst loading on the degradation of carbofuran was investigated using Degussa P-25 TiO_2 from 25 to 125 mg keeping all other parameters constant. The results are shown in Fig. 3. There is a steady increase in the rate of degradation up to 100 mg of the catalyst followed by decrease at higher loadings. The increase is due to increase in the catalyst surface area and light absorption [13]. The decrease at higher loading beyond the optimum level is due to decrease in the light penetration. Further, at higher catalyst loading, it is difficult to maintain the suspension homogeneous due to particles agglomeration, which decreases the number of active sites [14].
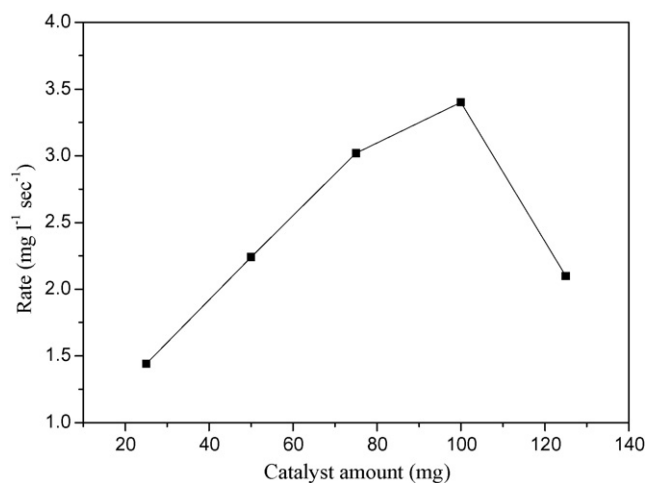
3.4. Effect of light intensity

The effect of light intensity was investigated from 16 to 64 W. The results reveal that the degradation rate increases with increase in the light intensity up to 64 W. The results are illustrated in Fig. 4. Electron–hole recombination is generally a very commonly encountered problem in photocatalysis. In addition, excitation of every catalyst particle by light irradiation at any instance cannot be expected. While increasing the intensity of incident light, the probability of excitation of electrons as well as the reexcitation of recombined electrons increase. Hence increase in the degradation rate is observed with increase in the intensity of incident light.

3.5. Mineralization

The extent of degradation and mineralization was followed using HPLC and TOC analyzer, respectively. The HPLC chromatograms show the degradation of pesticide into smaller fragments, which are subsequently mineralized completely. One hundred percent carbofuran was detected at 0 h irradiation
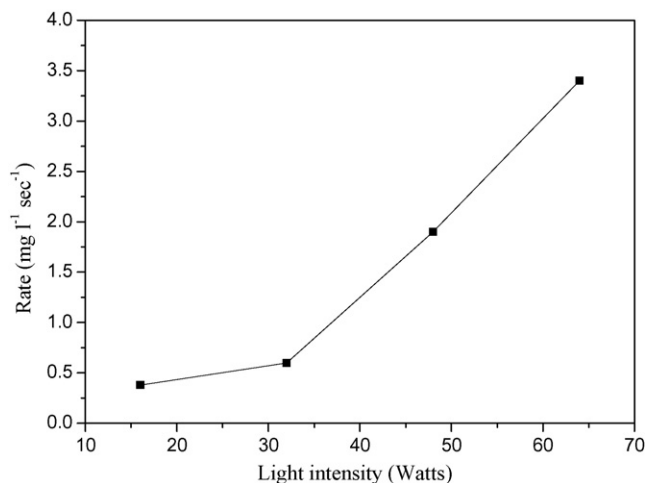

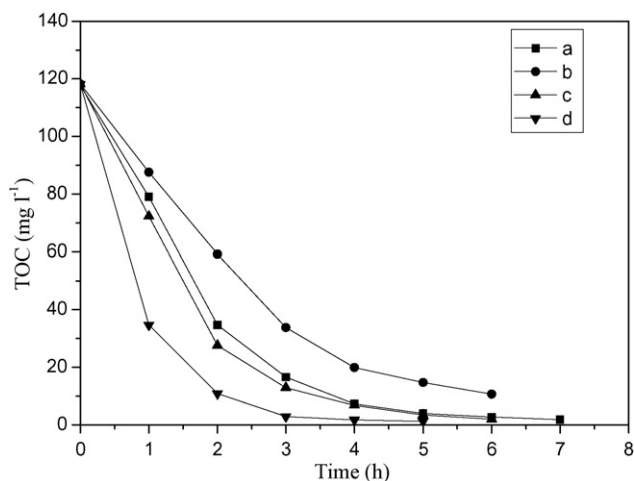Fig. 4. Effect of light intensity on degradation rate.

Fig. 5. Effect of irradiation time on total organic carbon (TOC). (Initial concentration of carbofuran: 200 mg l^{-1}, pH 7, catalyst amount: 100 mg/100 ml). (a) Catalyst: TiO$_2$; wavelength: 254 nm; diameter of reactor tube: 3 cm; (b) catalyst: ZnO; wavelength: 254 nm; diameter of reactor tube: 3 cm; (c) catalyst: TiO$_2$; wavelength: 365 nm; diameter of reactor tube: 3 cm; (d) catalyst: TiO$_2$; wavelength: 365 nm; diameter of reactor tube: 2 cm.

Fig. 6. UV–vis absorption spectrum of carbofuran.

whereas only 5% was observed at the end of 1 h. The carbofuran peak was not seen at the end of 2 h. But new peaks were observed at different retention times after 5 min irradiation confirming the formation of degradation products. These products were also degraded quickly and subsequently complete mineralization occurred. Complete mineralization of carbofuran was not achieved by anodic Fenton treatment [3] and photo Fenton reaction [15]. Though complete mineralization was reported over TiO$_2$ supported on glass plate it took 16 h [2]. In Fe (III) aqua complex only 70% mineralization was reported after 25 h irradiation [1]. In the present investigation TOC has decreased to 14% within 3 h and 2.2% in 6 h. The complete mineralization was achieved in 7 h as shown in curve a in Fig. 5. The rapid decrease in TOC within 3 h and a slow decrease afterwards indicate the formation of intermediates which are resistant to further degradation. The formation of NO$_3^-$ ions was confirmed by HPLC. Tennakone et al. [2] studied the photocatalytic mineralization of carbofuran using TiO$_2$ and reported NO$_3^-$, NO$_2^-$ and NH$_4^+$ ions in solution at the end of photolysis. These ions were also reported by other workers during the photomineralization of carbofuran [1,16]. The concentration of nitrate ions increases rapidly with increase in irradiation time. These ions inhibit the degradation by strong adsorption on the catalyst surface through hydrogen bonding interaction with hydroxylated surface of the catalyst [14]. Thus it decreases the number of active sites available for the adsorption of carbofuran and O$_2$. The photocatalytic degradation of nitrogen containing compounds such as amines [17] and amides [18] yields NO$_3^-$, NO$_2^-$ and NH$_4^+$ ions only without the evolution of gaseous nitrogen. The attack of hydroxyl radicals can induce cleavage of C–N bond of the substrate and hence the organic nitrogen is transferred into NO$_3^-$, NO$_2^-$ and NH$_4^+$ ions [17–20]. During the degradation of carbofuran, formation of significant amount of NH$_4^+$ was reported by Katsumata et al. [1]. Hence it is reasonable to assume that the NH$_4^+$ ion is eventually transformed into NO$_3^-$ and H$^+$ [17–19].
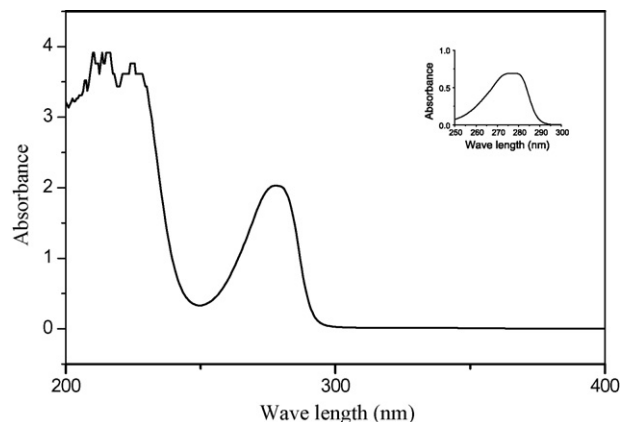
At the end of degradation process 1.25×10^{-4} mol l^{-1} of NO$_3^-$ ion was produced, corresponding to ca. 48% of the initial nitrogen in carbofuran. The carbamate group is the primary site of attack by the hydroxyl radical giving carbamic acid [16], which is a known unstable compound and hence decomposes rapidly to gaseous products such as methyl amine and carbon dioxide. The incomplete mass balance of nitrogen may be accounted by the fact that certain portion of nitrogen is evolved as volatile organic compound such as methyl amine. This incomplete mass balance has been frequently observed in a similar process [1,2].

3.6. Comparison of photocatalytic efficiency of TiO$_2$ and ZnO

The photocatalytic degradation of 100 ml of 200 mg l^{-1} carbofuran was performed at pH 7 with 100 mg TiO$_2$ or 100 mg ZnO. The initial rate of degradation of carbofuran with TiO$_2$

Table 1
The intermediates identified in the photodegradation of carbofuran

Product no.	Retention time (minutes)	MW (m/z)	Structure of intermediates
1	10.05	207	
2	9.879	164	
3	9.228	147	
4	5.6	120	

is higher than with ZnO. In addition, the TOC removal is also faster with TiO_2 than with ZnO (Fig. 5 curve b). The higher rate of degradation over TiO_2 supports the view that the surface mediated process is more predominant in the degradation reaction, thus the higher surface area of TiO_2 ($50 \, m^2 \, g^{-1}$) compared to that of ZnO ($10 \, m^2 \, g^{-1}$) can be accounted for the higher rate of degradation over TiO_2 than ZnO [14,21].

3.7. Mineralization of carbofuran with low-pressure mercury vapour lamps of wavelength 365 nm

The mineralization of carbofuran was also studied with lamp of wavelength 365 nm over TiO_2 (Fig. 5 curve c) and the result was compared with that of 254 nm. Though the mineralization rates apparently appear to be nearly equal for both the lamps, the mineralization rate at 365 nm is slightly higher than at 254 nm. Since the band gap excitation of electrons in TiO_2 with 254 nm can promote electrons to the conduction band with high kinetic energy, they can reach the solid–liquid interface easily suppressing electron–hole recombination in comparison to 365 nm. The observation of low rate for 254 nm is therefore unexpected. This may be accounted by considering partial absorption and wasting of the light of 254 nm by carbofuran itself. In order to verify this, the UV spectrum of carbofuran between 200 and 450 nm was scanned and is shown in Fig. 6.

It is evident from the UV–vis spectrum that carbofuran absorbs significant portion of light of wavelength at 254 nm. Hence the light energy at 254 nm may not be fully available for TiO_2 for excitation of electrons. Hence the absorption and wasting of the light of wavelength at 254 nm by carbofuran might be the actual cause for lesser rate of degradation than at 365 nm. The degradation process was also studied over two reactor tubes with different diameter (2 and 3 cm). The degradation was very fast in 2 cm diameter reactor tube than in 3 cm (Fig. 5 curve d). The photon absorption and the exposure of catalyst surface area are better in 2 cm diameter tube than in 3 cm. In addition, light penetration and hence utilization of photons by the catalyst will be enhanced in small diameter reactor tube. The complete mineralization was achieved quickly in 5 h at 365 nm using 2 cm diameter reactor tube.

3.8. Photodegradation products

The photodegradation products formed in 1 and 3 h irradiations were analyzed using GC–MS. Table 1 summarizes the degradation products and their molecular weights after 1 h irradiation. The products were identified to be 2,3-dihydro-2,2–dimethylbenzofuran-7-yl carbamate (1), 2,3-dihydro-2,2–dimethyl-7-hydroxy benzofuran (carbofuranphenol) (2), 2,3-dihydro-2,2-dimethyl benzofuran (3) and
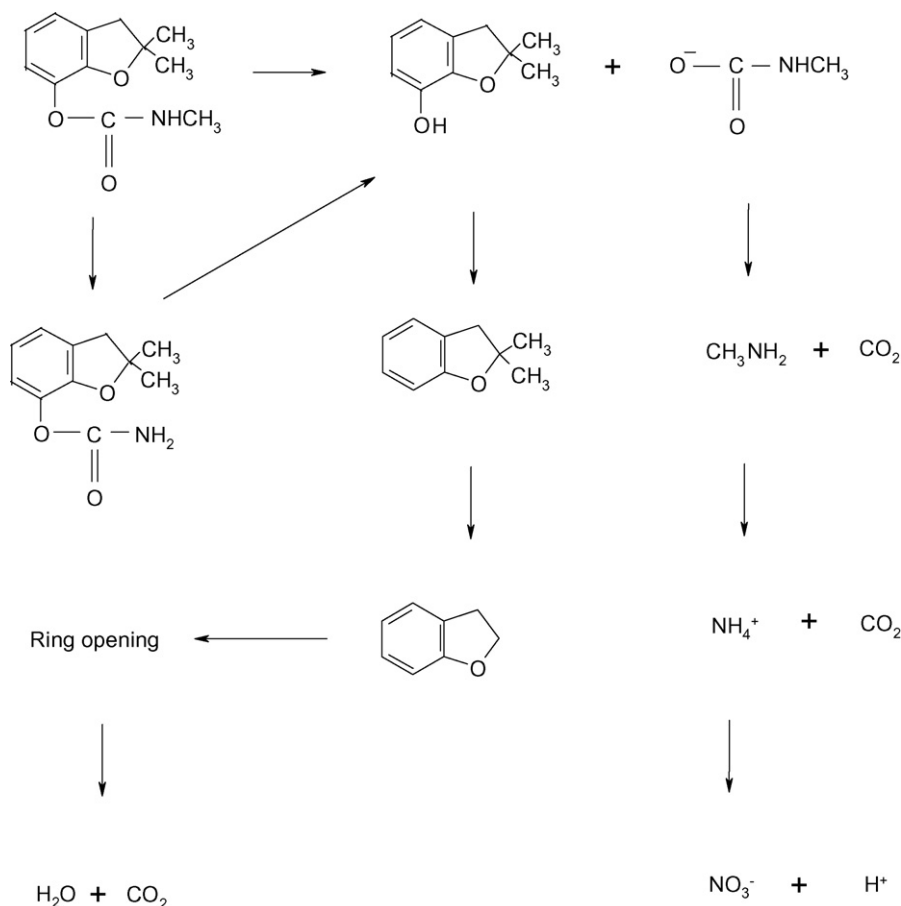
Scheme 1. Proposed pathway for the degradation of carbofuran by TiO_2.

2,3-dihydro-benzofuran (4). The products 3 and 4 were only detected in the 3 h irradiated sample and the absence of other fragments observed during the initial irradiation period show the progressive degradation of carbofuran. Based on the intermediate products listed in Table 1 and earlier reports on the products [1,3,16] the possible degradation pathway is proposed as shown in Scheme 1. The degradation product 2,3-dihydro-2, 2–dimethyl-7-hydroxy benzofuran (carbofuranphenol) (2) is also obtained by the base hydrolysis of carbofuran [12]. The carbamate group is the primary site of attack by the hydroxyl radical giving carbamic acid [16], which is a known unstable compound and hence decomposes rapidly to gaseous products such as methyl amine and carbon dioxide. The breaking down of benzene ring and subsequent mineralization leading to water and carbon dioxide could be visualized by the decrease in TOC during the photocatalytic process.

4. Conclusions

The photocatalytic degradation of carbofuran in aqueous medium with Degussa P-25 TiO_2 and ZnO at wavelength 254 nm using low pressure mercury vapour lamps was investigated. TiO_2 showed higher activity than ZnO. Complete mineralisation of carbofuran with TiO_2 was observed within 5 h under optimal conditions. Comparison of rate of degradation of carbofuran at two different wavelengths, 254 and 365 nm, shows slightly higher rate of degradation for 365 nm than 254 nm, contrary to the expectation of lower rate for 365 nm than 254 nm. It is due to partial absorption and wasting of light at 254 nm by carbofuran. This study concludes that in selecting suitable lights for effective photocatalytic mineralization, light absorption behavior of the pollutants must be given due consideration. This study reveals the formation of four intermediates in the degradation of carbofuran. The plausible degradation pathway is also proposed based on the products.

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