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TiO_2-BASED HETEROGENEOUS PHOTOCATALYTIC TREATMENT COMBINED WITH OZONATION FOR CARBENDAZIM DEGRADATION

R. Rajeswari , *S. Kanmani

Centre for Environmental Studies, Anna University, Chennai, India

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ABSTRACT

The degradation of pesticide Carbendazim was investigated by combination of TiO_2-based photocatalysis and ozonation. A batch annular photoreactor has been used for carrying out the combined process and the influence of TiO_2 concentration, ozone dose and pH were investigated. The results showed that the removal rate increased with increase in ozone dosage upto 0.48 g/h and decreased above 1g/L of TiO_2. At optimum pH=6, with 1g/L TiO_2 and with 0.48g/h ozone dose, 88% COD removal was achieved in 3 hours by the combined photocatalytic ozonation process, where as 54% and 67% COD removal was observed with each photocatalysis and ozonation process, respectively. BOD_5/COD ratio was enhanced to 0.38 and TOC removal was 80% in 180 min of combined treatment. Carbendazim was quickly degraded by the combined photocatalytic ozonation process and followed pseudo-first order kinetics. The kinetic study showed that degradation rate constant of Carbendazim with TiO_2/UV/O_3 to be 1.5 times higher than that & O_3 with the same ozone dose and 2.2 times higher than that of TiO_2/UV. A mechanism involving the formation of an ozonide radical previous to the generation of hydroxyl radicals is suggested to explain the synergistic effect between ozone and TiO_2 under illumination. The laboratory study has also demonstrated that a combination of TiO_2-based photocatalysis and ozonation will overcome the disadvantage of the selectivity of ozonation and the lower efficiency of TiO_2 photocatalysis.

Keywords: Pesticide, Photocatalysis, Ozonation, Photocatalytic Ozonation, Synergistic effect, Carbendazim

INTRODUCTION

Water contamination is mainly caused by industrial effluents, agricultural runoff and chemical spills which contain several non-biodegradable substrates that can be harmful to the environment. Their toxicity, stability to natural decomposition and persistence in the environment have been the cause of much concern to the society and regulation authorities all around the world. Although various industries are responsible for contributing these hazardous organic wastes into water resources, the pesticide industry is of major concern. Important causes of pesticide water pollution are effluents from agricultural runoff, from formulating or manufacturing pesticide plants and bottles and container washings. Since these pesticides pose a high threat for aquatic systems, it is of great importance to find the effective method for their elimination from different sources (Chiron *et al*., 2000)

Carbendazim, an important systemic fungicide with wide range of activity is one of the most commonly used pesticides in India. It inhibits a wide variety of fungi and is also toxic (Roy, 2002). Because of its extensive use, Carbendazim accumulates as a pollutant in water resources and it is of great interest to investigate the processes leading to its elimination. Generally, conventional biological treatment is not very effective for pesticides removal because of their toxicity. Instead, activated carbon adsorption or solar evaporation is generally practiced. However, new environmental laws may consider the spent adsorbents and sludge as hazardous waste and require further treatment. Consequently, intensive research for novel technologies that pursue easy degradation of such substances with higher efficiency has been stimulated.

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*Corresponding author: *skanmani@hotmail.com*
Tel: 091 44 22203196, Fax: 091 44 22354717

Among the many processes proposed and /or being developed for the destruction of organic contaminants, photocatalytic process involving TiO_2 particles under UV illumination has shown to be potentially advantageous and is useful in the treatment of wastewater pollutants (Gogate and Pandit, 2004). The fundamental mechanism of photocatalysis consists in the generation of electron-hole pair, which determines the occurrence of redox reactions of species adsorbed on the photocatalyst surface. In this process, O_2 is widely used as an additional oxidant. The disadvantage is the slow electron transfer from TiO_2 to O_2 and that mineralization requires longer time (Akawat *et al*., 1999).

In order to improve the performance of photocatalytic process, different strategies have been used. The efficiency of TiO_2 photocatalytic process has been improved by doping with transition metals (Di Paola, 2002), by using photosensitizers (Mele *et al*., 2003) or by adding oxidant species such as H_2O_2 (Muneer *et al*., 1999), Fe^{2+} ions (Pignatello, 1992), peroxodisulfate and periodate ions (Oyama, 2000) or O_3 (Kopf *et al*., 2000). On the other hand, the use of ozone for the destruction of organics in water is considered as a well known water treatment technique (Buhler, 1984). Ozone is a powerful oxidant ($E^\circ = 2.07V$) and reacts with many compounds via direct or indirect reactions. Indirectly, ozone can react by hydroxyl radical ($E^\circ = 2.8V$) which is a powerful and nonselective oxidant and can react with almost all organic compounds.

The similarity between the mechanisms of destruction in the case of different oxidation techniques indicates that appropriate combination of these oxidation systems could give better performance, as compared to individual processes and some of the drawbacks of the individual techniques can be eliminated by some characteristics of other techniques. The efficacy of these processes depends strongly on the rate of generation of the free radicals and their utilization by organic molecules.

Photocatalytic ozonation is one such emerging new technology which uses the combination of TiO_2 photocatalysis and ozonation. It has been recently studied in treating dibutyl phthalate (Li *et al*., 2005), oxalate ions (Addamo *et al*., 2005), carboxylic acids (Ilisz *et al*., 2004) and phenolic wastewaters (Gimeno *et al*., 2008). Further, a review on different compounds degraded by using photocatalytic ozonation has been published (Agustina *et al*., 2005) and the results showed that the combination of two methods gave the highest removal of organics in effluent in shorter duration.

Photocatalytic ozonation is qualitatively and quantitatively different from the well known photocatalytic oxidation with oxygen. The higher oxidation rate is probably a photocatalytic induced decay of ozone initiated by the combination of TiO_2 and UV illumination (Kopf *et al*., 2000). When ozone is present in photocatalytic suspension, in addition to the homogeneous pathways of direct ozonation, the role of ozone as an electron trap must be considered. In the presence of TiO_2 and near UV radiation, adsorbed ozone acts as a very strong electrophilic agent generating ozonide radical where further reactions produce eventually hydroxyl radicals in the adsorption layer(Addamo *et al*., 2005).

$$TiO_2 + h\nu \longrightarrow e^- + h^+ \qquad (1)$$

$$O_{3\,(ads)} + e^-_{cb} \longrightarrow O_3^{-\cdot} \qquad (2)$$

$$O_3^{-\cdot} + H^+ \longrightarrow HO_3^{-\cdot} \qquad (3)$$

$$HO_3^{-\cdot} \longrightarrow HO^{\cdot} + O_2 \qquad (4)$$

The e^-_{cb} in equation 2 denotes the electrons in the conduction band. In TiO_2 photocatalysis, electrons are exited from valence band to conduction band and the ozone which is adsorbed on the TiO_2 takes up theconduction band electrons and becomes ozonide radical anion as mentioned in equation 2. The above reported mechanism gives rise to the formation of one hydroxyl radical per each trapped electron. In conventional photocatalytic processes, O_2 is used as the oxidant compound. The disadvantages of using O_2 as electron trap are the slow electron transfer from TiO_2 to O_2 and the fact that three electrons are needed for the generation of hydroxyl radicals.

$$3O_2^{\cdot -}{}_{(ads)} + 3e^-_{cb} \longrightarrow 3O_2^{\cdot -} \qquad (5)$$

$$2O_2^{\cdot -} + 2H_2O \longrightarrow 2HO_2^{\cdot} + 2OH^- \qquad (6)$$

$$2HO_2^{\cdot} \longrightarrow O_2 + H_2O_2 \quad (7)$$

$$H_2O_2 + O_2^{\cdot -} \longrightarrow HO^{-} + HO^{\cdot} + O_2 \quad (8)$$

Consequently, when the photocatalyst is irradiated in the presence of ozone, a greater number of hydroxyl radicals are produced. Ozone therefore acts as a powerful oxidant in place of oxygen mainly owing to the fact that ozone is more electrophilic than O_2 towards electron photogenerated onto the TiO_2 surface. Therefore, when the catalyst is irradiated in the presence of ozone, a greater amount of hydroxyl radicals is formed with respect to that produced in the presence of O_2.

In this paper, the combined effect of $TiO_2/UV/O_3$ on the degradation of Carbendazim was studied and the effect of varying experimental parameters such as TiO_2 concentration, ozone dosage and pH were also investigated. The synergistic effect of ozonation on TiO_2 photocatalysis was evaluated and compared with individual techniques.

MATERIALS AND METHODS

For the experimental runs, a pyrex annular photoreactor has been used. The photoreactor containing 500mL of aqueous suspension was provided with ports in the upper part for inlet and outlet of ozone and at the lower part to withdraw aliquots of reacting suspension. A medium pressure mercury lamp of 15W was immersed in axial position inside the photoreactor. The photon flux emitted by the lamp has its maximum value at 254 nm. TiO_2 (Degussa P25) was used as photocatalyst without any further preliminary treatment in different concentrations of 0-2 g/L. Ozone was produced by feeding synthetic air to the ozone generator (Indiozone, India) and was varied from 0.12 g/h to 0.52 g/h. The initial pH of the Carbendazim solution was 5.8 and was adjusted using 0.1N H_2SO_4 or 0.1N NaOH. The temperature of the suspension was maintained at 20±1° C. The slurry mixed by magnetic stirrer was allowed to attain steady state in the dark for 30 min. after which ozone was passed through the reactor. The unreacted ozone was absorbed by potassium iodide traps outside the reactor. For this study, the concentration of TiO2 was varied from 0 g/L to 2 g/L and the pH from 3 to 9. Aliquots of samples were withdrawn at specified intervals of time. The photocatalyst was immediately filtered by centrifugation and the filtrate was taken for analysis.

The percentage removal of Carbendazim was monitored by measuring the absorbance on Spekol 1200 UV-Vis spectrophotometer. The UV-Vis spectrum of aqueous solution of Carbendazim changes according to the pH of the solution. Maxima can be noted at 207 nm and 285 nm for the molecular form at pH=6. The amount of ozone generated was determined by iodometry. The pH of the solution was measured by using digital pH meter, DI-707 (Digisun electronics, Hydrabad). COD and BOD analysis were carried out as per Standard Procedure (APHA, 2005). The TOC was measured using Total Organic Carbon Analyser (Shimadzu, Japan).

RESULTS

Effect of initial catalyst concentration

In slurry photocatalytic processes, catalyst dosage is an important parameter. Thus, in a preliminary series, the influence of initial catalyst concentration on the photocatalytic ozonation of pesticide was examined. From Fig.1, it was observed when TiO_2 concentration was increased from 0 g/L to 1g/L, an increase in removal rate was found. Nevertheless, a further rise in TiO_2 concentration (2g/L) did not lead to corresponding enhancement in removal rate; infact, it was reduced.

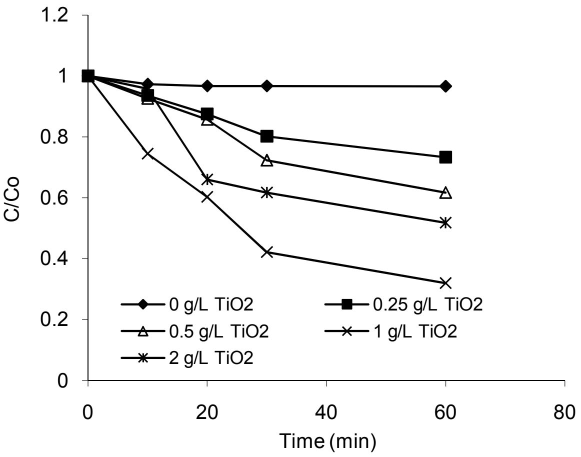

Fig.1: Effect of initial catalyst concentration on photocatalytic ozonation
(Carbendazim= 40 mg/L; Ozone dose= 0.48 g/h; pH= 6; TiO_2= 0-2 g/L)

Effect of ozone dosage

To find out the optimal ozone dosage required for the degradation of Carbendazim, the ozone dosage was varied from 0 g/h to 0.52 g/h. The removal rate was found to increase linearly with increase in ozone dosage (as observed from Fig.2) and becomes almost similar at 0.48 g/h and 0.52 g/h.

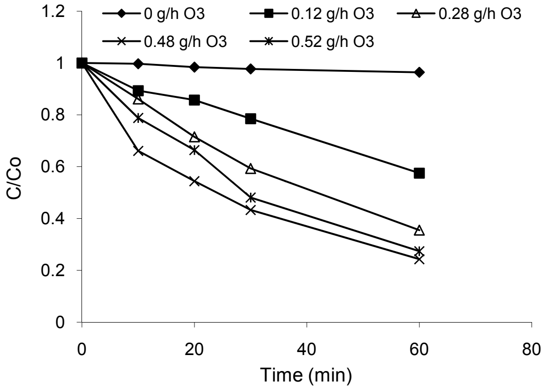

Fig. 2: Effect of ozone dosage on photocatalytic ozonation (Carbendazim= 40 mg/L; TiO_2= 1 g/L; pH= 6; Ozone dose= 0-0.52 g/h)

Effect of pH

Since both the TiO_2/UV process and O_3 process show pH dependence, it is important to examine the influence of pH on the degradation of Carbendazim in the combined $TiO_2/UV/O_3$ process which is represented in Fig.3. Here, maximum degradation was observed at pH=6. The results of Carbendazim degradation for 60 min at pH=6 using combination approach (69.2%) was more than 1.2 times higher than the best results of ozonation at pH=9 (60.1%) and more than 1.6 times higher than the fastest degradation (42.8%) obtained by applying TiO_2 photocatalysis at pH=6.

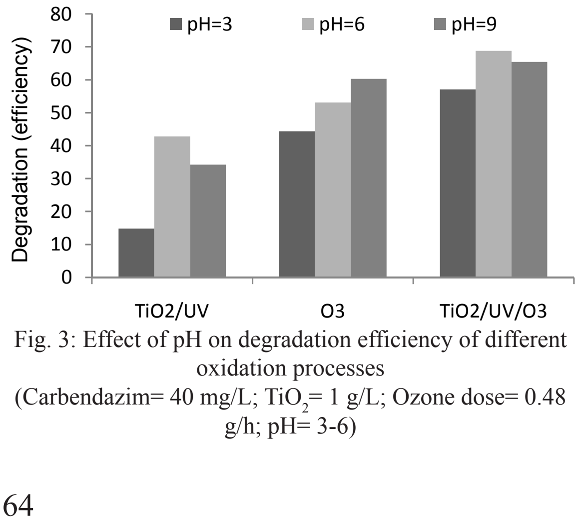

Fig. 3: Effect of pH on degradation efficiency of different oxidation processes
(Carbendazim= 40 mg/L; TiO_2= 1 g/L; Ozone dose= 0.48 g/h; pH= 3-6)

Synergistic Effect of photocatalytic ozonation

Different experiments using O_3, TiO_2/UV and $TiO_2/UV/O_3$ have been conducted to asses the synergistic effect or increased degradation achieved using photocatalytic ozonation. Fig.4 shows the kinetic results obtained for these three processes at different time intervals. For all these experiments, the ozone flow was maintained at 0.48 g/h with 1g/L of TiO_2 and 40mg/L of Carbendazim. The rate constants and the COD removal achieved in 180 min duration are shown in Table 1. The kinetic study showed that degradation rate constant with $TiO_2/UV/O_3$ was 1.5 times higher than O_3 with same concentration and 2.2 times higher than that of TiO_2/UV.

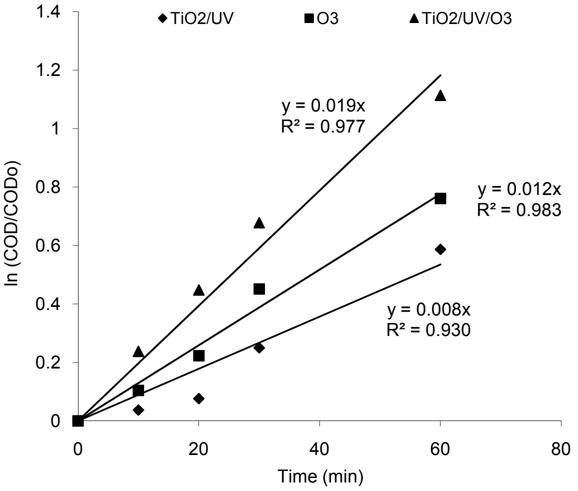

Fig. 4: Study of kinetics for different oxidation processes

Table 1: Rate Constants and COD removal efficiency of different oxidation processes

Oxidation system	BOD_5/COD (initial)	BOD_5/COD after 180 min of oxidation
TiO_2/UV	0.10	0.24
O_3	0.12	0.30
$TiO_2/UV/O_3$	0.12	0.38

Mineralization studies

To asses the mineralization efficiency of photocatalytic ozonation process, the TOC values were measured at different time intervals for 40mg/L of Carbendazim. Fig.5 shows the mineralization efficiency and the decrease in concentration of Carbendazim with time. 80% mineralization with 97% removal of pesticide was achieved by photocatalytic ozonation in 180 minutes.

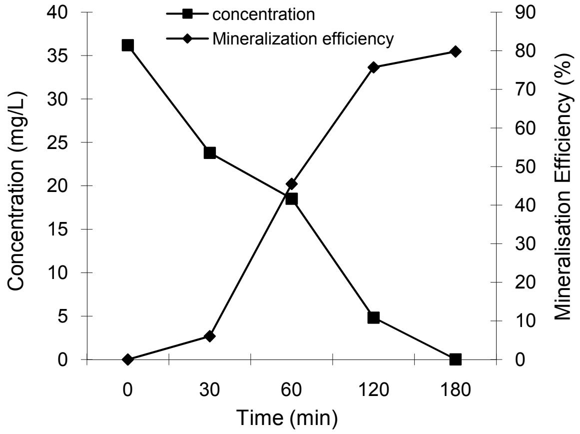

Fig. 5: Mineralization and removal of Carbendazim by photocatalytic ozonation (Carbendazim= 40 mg/L; TiO_2= 1 g/L; Ozone dose= 0.48 g/h; pH= 6)

Biodegradability studies

The most extended way to qualify biodegradability is the assessment of BOD_5/COD ratio. It is commonly accepted that a wastewater is completely biodegradable when that ratio is about 0.4, while a value between 0.3-0.4 corresponds to partial biodegradability (Sarria *et al.*, 2002). Thus BOD_5 and COD analysis were also carried out to find out the extent of biodegradability achieved by photolytic ozonation. The results were evaluated as BOD_5/COD ratio, representative of the solution biocompatibility and are summarized in Table 2. As it can be depicted from Table 2, for photocatalytic ozonation, the ratio reached 0.38 which was higher than that recorded in the initial solution.

Table 2: Biodegradability of different oxidation systems

Oxidation system	BOD_5/COD (initial)	BOD_5/COD after 180 min of oxidation
TiO_2/UV	0.10	0.24
O_3	0.12	0.30
TiO_2/UV/O_3	0.12	0.38

DISCUSSION

The gradual increase in Carbendazim removal with increase in catalyst concentration was attributed due to increase in the surface area and thus the number of active sites. When the catalyst concentration is too high, the excess catalyst might lead to a shielding effect on the penetrating radiation. Increased turbidity of the solution impedes further penetration of light into the reactor. Similar types of results have also been reported (Gimeno *et al.*, 2008).

The deviation from linear increase at higher ozone dosage was due to the fact that at this point, the number of ozone molecules was already high enough to extract completely the photogenerated electrons from the catalyst surface. The additional increase of flow rate of ozone would no longer contribute to increase the removal rate and escapes out as unreacted (Cernigoj *et al.,* 2007).

In case of ozonation, the degradation rate was found to increase with increase in pH. This may be due to the fact that increasing pH will accelerate O_3 decomposition to generate hydroxyl radical, which destroys the organic compounds more effectively than molecular O_3 does (Kasprzyk *et al.*, 2003). For photocatalytic process, generally pH has varied effect on the process and it is expected that increase or decrease in the pH should affect the rate of degradation as adsorption varies with pH. Here, maximum degradation was observed at pH=6. For the combined process, the maximum degradation rate was obtained by simultaneous application of both the methods at neutral pH values (Muller *et al.*, 1998).

The COD removal achieved in 180 minutes with TiO_2/UV/O_3 process was higher compared to TiO_2/UV and O_3 processes which proves the synergistic effect in combined process. However, the question arises whether this is just consequence of two independent AOPs (TiO_2/UV + O_3) contribution or there is some synergistic effect of ozone on photocatalysis. If the sum of degradation rate constants of TiO_2/UV + O_3 is smaller than degradation rate constants of TiO_2/UV/O_3, the synergistic effect will be easily proven. Here, when carbendazim was degraded using the combination of photocatalysis and ozonation, degradation efficiency was considerably higher (0.0197 min^{-1}) than the sum of that using individual processes alone (0.0109 min^{-1}) which implies synergistic effect between photocatalysis and ozone. The reason for this synergistic effect is explained based on the mechanism of the reactions involved. Similar results have also been reported for the degradation of 2, 4 D (Giri *et al.*, 2008).

The removal rates for 2,4 D and TOC in O_3/UV/TiO_2 were respectively 1.5 and 2.4 fold larger than the summation of the corresponding values in O$_3$ and UV/TiO$_2$. The decomposition of aliphatic carboxylic acid has been reported (Ilisz *et al*., 2004) in which the combined process was proved to be most effective for degradation of all acids compared to ozonation and photocatalysis.

Slow rate of mineralization compared to removal of pesticide might be due to the formation of stable intermediates. The positive efficiency of photocatalytic ozonation on biodegradability was evident from the increase in the BOD$_5$/COD value. Further increase in this ratio may be obtained when the reaction time is increased further, so that the organic matter is completely mineralized.

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