

Degradation of Carbaryl by Photolytic Ozonation

R. Rajeswari* and S. Kanmani

Centre for Environmental Studies, Anna University, Chennai – 600 025, India

✉ rajikanna99@yahoo.co.in

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Abstract: The degradation of Carbaryl, a frequently used carbamate derivative pesticide, was carried out in batch reactors by photolytic ozonation. The influencing factors such as pH, pollutant concentration and ozone dosage were studied to optimize the reaction conditions. The maximum COD removal of 78.5% was achieved in three hours at alkaline pH 9. Increase in ozone dosage from 0.12 g/h to 0.48 g/h increased degradation rate. The apparent pseudo first order rate constant for photolytic ozonation and ozonation processes were found to be 0.0209 min^{-1} and 0.0139 min^{-1} respectively which indicated the presence of highly reactive hydroxyl radicals in photolytic ozonation. Complete mineralization needs longer ozonation time and only 48% TOC removal was achieved in three-hour duration. BOD_5/COD ratio increased from 0.02 to 0.38 which facilitates coupling with secondary biological treatment.

Key words: Pesticide, carbaryl, photolytic ozonation, biodegradability.

Introduction

The presence of highly biorecalcitrant organic contaminants such as pesticides in aquatic environment due to industrial and intensive agricultural activities is of particular concern all over the world. In recent years, the scientific community has shown a great concern about the possible adverse effects of these pollutants on human health and on the equilibrium of the ecosystems.

In response to the growing risk of environmental hazards associated with these pesticides, it is advisable to develop technologies that promote the easy degradation of these biorecalcitrant organic compounds. Ozonation is a promising technique in water treatment for the removal of water pollutants, odours, colour and tastes and increasing the biodegradability through the degradation of big molecular weight contaminants to lower molecular weight compounds as a preparation for the subsequent secondary biological treatment. Although ozone is known to be a powerful pre-oxidant, hydroxyl radicals in comparison to ozone have a higher oxidation potential and can react more rapidly with most organic compounds (Alvares et al., 2001; Hoigne, 1998). Further,

ozone is also highly selective which does not have potential to oxidize the intermediates. Hence, it is necessary to improve the efficiency of ozonation process in order to overcome the disadvantage of expensive chemical oxidation reaction due to the high production cost of ozone. Oxidation processes based on ozonation methods aimed at an enhancement of its efficiency have recently received much attention (Oyama, 2000).

Photolytic ozonation (UV/O_3), which aims to improve the efficiency of ozonation, is considered to be an Advanced Oxidation Process (AOP) that applies ozonation and UV irradiation simultaneously to the target compounds, and converts these compounds completely to a simple inorganic species, such as carbon dioxide and water. UV/O_3 thus has the potential for being an environmentally clean process for treating organic contaminants and has attracted attention at present for a wide range of wastewater treatment applications. However, the initial and operating costs of photolytic ozonation are still relatively expensive compared to traditional treatment technologies. Therefore, the determination of optimum operational conditions is one of the primary concern to improve the efficiency of the process for the future development and potential application to different contaminants, at the reduced cost.

*Corresponding Author

The objective of this study is to investigate the effects of pH, pollutant concentration and ozone dosage at various experimental conditions and also to study the extent of mineralization and biodegradability achieved by photolytic ozonation of commercial grade carbaryl, a widely used insecticide in India.

Materials and Methods

Commercial grade carbaryl (Sevin), a carbamate insecticide, was purchased from Sundaram Agro Industries, Chennai. All analytical grade reagents H_2SO_4 , NaOH , KI , starch and sodium thiosulphate were purchased from Merck. For the experimental runs a pyrex batch photoreactor of cylindrical shape has been used. The schematic representation of experimental setup is shown in Figure 1. The photoreactor of capacity 500 mL was provided with inlet and outlet for ozone flow. A medium pressure mercury lamp (150 W/254 nm) was immersed in axial position inside the photoreactor. Ozone was generated from dried atmosphere air by a prototype corona discharge generator (Indiozone, India). Carbaryl solutions were ozonized in the presence of UV at the desired pH and at room temperature by bubbling O_3 /air mixture with sintered glass disperse that released the gas from the bottom to the top of the reactor. The samples were collected at regular intervals of time for analysis. Excess ozone leaving the reactor was trapped by two sequential bubblers containing 2% KI aqueous solution.

Results and Discussion

Effect of pH

To study the effect of pH, the reaction was performed at different initial pH ranging from 3 to 9 with 40 mg/L of

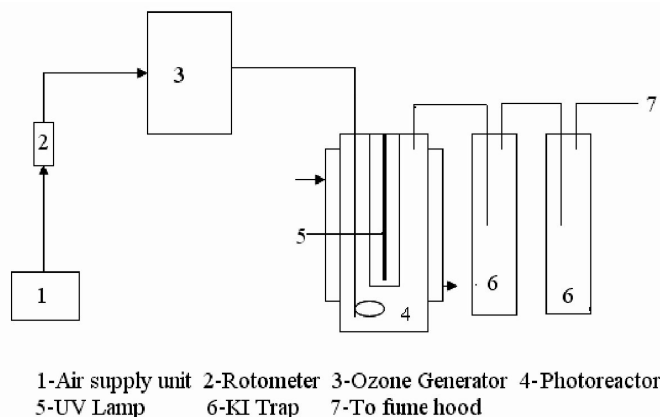
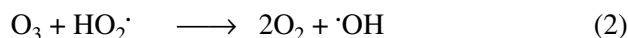
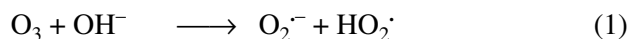
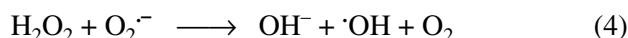
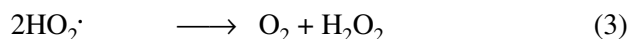


Figure 1: Schematic representation of photolytic ozonation reactor.

carbaryl. Generally, O_3 reacts with organic compounds in water directly via a molecular O_3 pathway or indirectly via hydroxyl radical pathway (Hoigne, 1998). At higher pH, the formation of hydroxyl radicals and subsequently the radical pathway would be enhanced as long as there were no hydroxyl radical scavengers present in the solution. It is known that at alkaline pH, O_3 molecules react with hydroxyl ions eventually producing the strong oxidant hydroxyl radicals (Kasprzyk Hordern et al., 2003).



Or alternatively:



Here, under the experimental conditions used, the degradation rate of carbaryl increases with increase in pH and the maximum degradation observed was 60.7% at pH 9 as shown in Figure 2 which proves that the reaction had taken radical pathway for degradation.

Effect of Pollutant Concentration

To study the effect of initial pollutant concentration on ozonation, the reactions were carried at different initial concentrations ranging from 20 mg/L to 100 mg/L at pH 9 and the results are shown in Figure 3. The linear increase in the initial degradation rate has shown that the number of oxidant molecules available for initial reaction with the pesticide molecules has been still high and that the

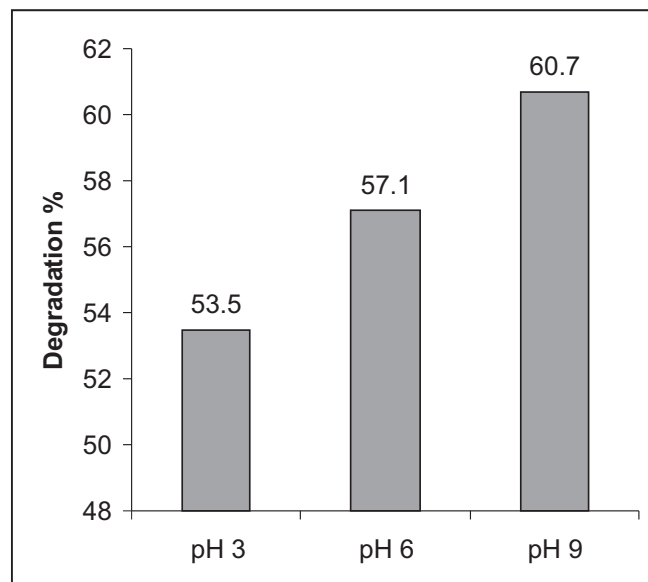


Figure 2: Effect of pH.

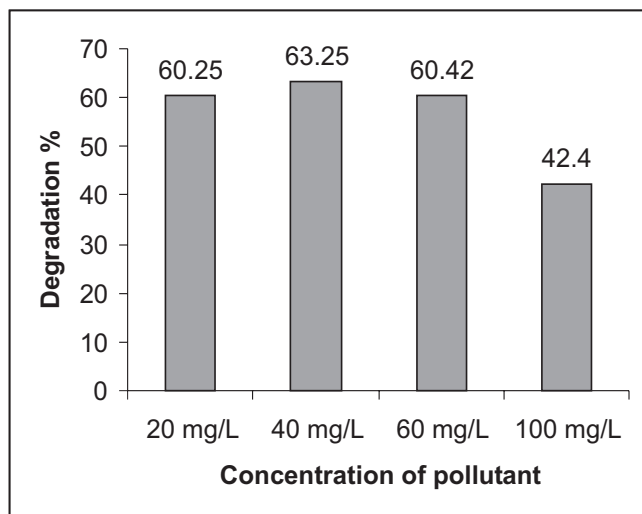


Figure 3: Effect of pollutant concentration.

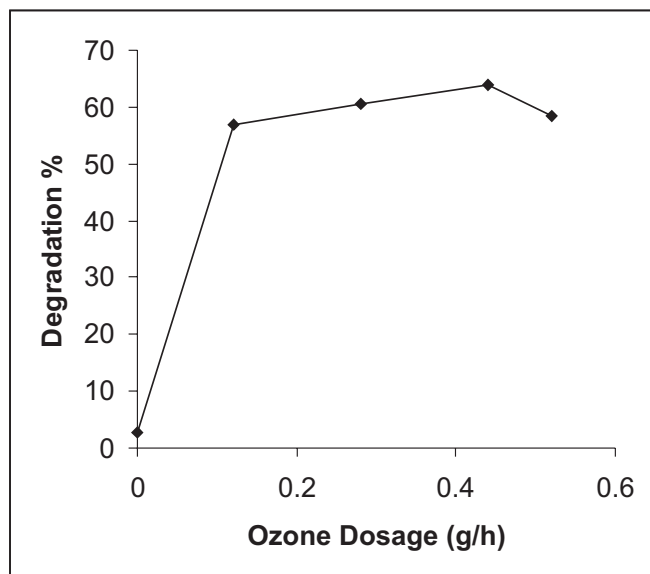


Figure 4: Effect of ozone dosage.

saturation point, where the pesticide molecules outnumber the oxidant molecules at the first instance, has not yet been reached till 60 mg/L. For 40 mg/L of carbaryl, with 0.28 g/h O_3 , 63.2% degradation was observed at pH 9.

Effect of Ozone Dosage

To study the effect of influent ozone dosage, experiments were carried out by modifying the influent ozone dosage from 0 g/h to 0.52 g/h and the results are presented in Figure 4. The figure clearly shows that increase of influent applied ozone dosage would result in the increased degradation rate of carbaryl from 56% to 64%. However,

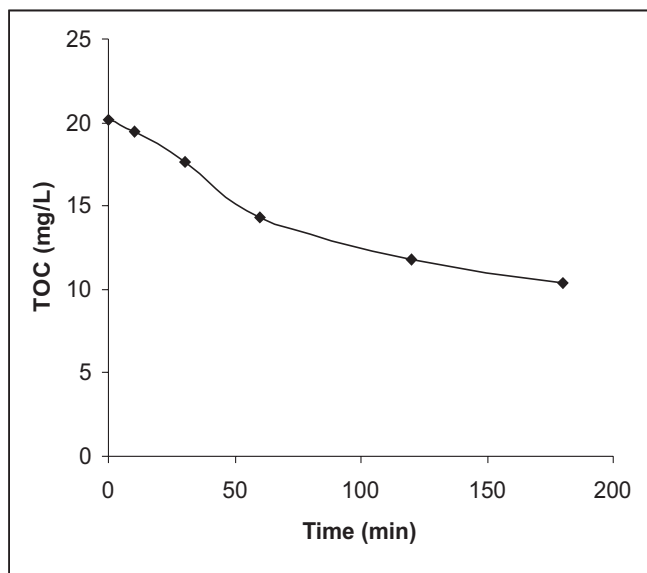


Figure 5: TOC removal by photolytic ozonation.

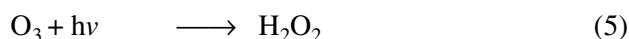
higher ozone dosage did not increase the degradation rate appreciably and ozone escapes out at faster rate without reacting with the pollutants (Benitez et al., 1991).

Mineralization Studies

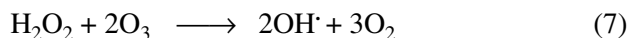
In order to study the mineralization extent by photolytic ozonation, the TOC analysis of carbaryl was conducted at different time intervals. Figure 5 shows the residual TOC of carbaryl where gradual mineralization was observed. Generally mineralization proceeds more slowly and in the absence of UV light the mineralization efficiency was 34% which increased to 48% in the presence of UV light. The slow degree of mineralization may be attributed due to the formation of intermediates.

Comparison of Photolytic Ozonation/Ozonation

The presence of UV radiation during the ozonation of organic compounds has been reported to increase the rate of oxidation by 10^{-10^4} times (Oyama, 2000). Ozone absorbs UV radiation in 200-600 nm range, resulting in the reversal of the O_3 formation reactions, and establishments of a steady state concentration. To compare the efficiency of photolytic ozonation with ozonation alone, the reaction was performed in the absence of UV light. Figure 6 shows clearly that UV/ O_3 has better efficiency compared to ozonation. This enhancement in the degradation rate can be explained by considering the reactions that occur in this AOP. Ozone absorbs UV radiation and produces H_2O_2 as shown in equation 5 (Peyton et al., 1982).



And then, there is a photolysis of H_2O_2 to generate hydroxyl radicals as shown in equation 6.



H_2O_2 also accelerates the ozone decomposition into hydroxyl radicals as shown in equation 7 (Staehelin and Hoigne, 1982). A least square regression analysis on Figure 6 gave the values of rate constant listed in Table 1. Correlation coefficient >0.98 in all cases confirm the goodness of the assumed kinetics for the ozonation. The contribution of the radical pathway in the photolytic ozonation explains the increase of the apparent pseudo first order rate constant by a factor of 2 when compared to conventional ozonation.

Biodegradability Studies

The most extended way to express biodegradability is the assessment of the 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). Figure 7 shows the BOD_5/COD ratio of the pesticide before and after photolytic ozonation. $\text{BOD}_5/$

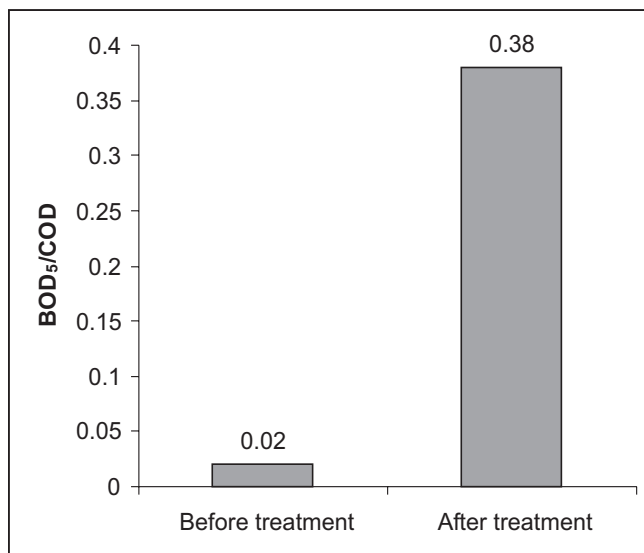


Figure 7: Biodegradability studies on carbaryl.

COD value reaches 0.38 after the treatment, which suggests that the wastewater has become partially biodegradable.

Conclusion

The results of this study indicate that for the treatment of pesticide formulation wastewater, photolytic ozonation can be effectively applied. The reaction was favourable at alkaline pH condition, which enhances the hydroxyl radical ion formation. Further, increase of ozone dosage increased removal rate, but more amount of ozone was unused at higher dosages, which is the main factor to be taken for improvement. The contribution radical pathway explains the enhancement in the rate of photolytic ozonation when compared to conventional ozonation.

Table 1: Kinetic results of photolytic ozonation/zonation

S. No.	Process	% Removal	$K \text{ (min}^{-1}\text{)}$	R^2
1.	UV/ O_3	97.7	0.0209	0.9940
2.	O_3	92.0	0.0139	0.9860

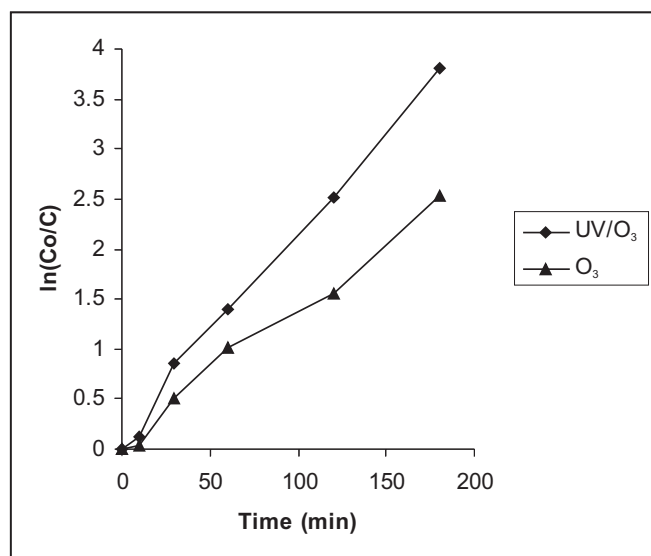


Figure 6: Comparison of photolytic ozonation and ozonation.

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