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Comparative study on photocatalytic oxidation and photolytic ozonation for the degradation of pesticide wastewaters

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ABSTRACT

Photocatalytic oxidation and photolytic ozonation have been employed to remove carbendazim, a commonly used fungicide. The effect of catalyst dosage, ozone dosage, and initial solution pH on the reaction was investigated. In the photocatalytic oxidation process, the optimum catalyst dosage and pH were found to be 1 g/L and 4, respectively. In the photolytic ozonation process, the optimum ozone dosage was 0.48 g/h and pH was 9. The pseudo first order rate constants achieved were 0.0212 min^{-1} for photolytic ozonation and 0.0103 min^{-1} for photocatalytic oxidation. Both treatment processes were compared based on the pesticide removal and mineralization. The results showed that photolytic ozonation performed better with 98% removal and 85.4% mineralization was achieved, whereas only 85% removal and 62.2% mineralization in photocatalytic oxidation after a treatment time of 3 h.

Keywords: Photocatalytic oxidation; Photolytic ozonation; Pesticide; Carbendazim

1. Introduction

The occurrence of emerging or newly identified contaminants in our water resources is of continued concern for the health and safety of consuming public. Water polluted with pesticides constitutes an increasing environmental pollutant, mainly in places such as India, where intensive agriculture is an important activity. During the last decade, the unregulated manufacture and usage of pesticide chemicals have had much more deleterious effects on our environment, than the benefits it bestowed to the society. So the use and manufacture of any pesticide is now a subject matter of controversy, not only in India but as well in abroad. Further, from pesticide manufacturing and formulating industries undesirable compounds are being released, knowingly or unknowingly, into the aquatic environment and because of the persistence and potential adverse effects the presence of pesticides has been recognized as a major issue in many countries [1]. Due to their chemical characteristics, they resist in variable degree the photochemical, chemical and bio-chemical degradation [2]. The current wastewater treatment methods adopted in industries are solar evaporation or biological treatment systems which are not effective in elimination of these different classes of pesticides.

In the last decade, a lot of research has been addressed to a special class of oxidation technique known as advanced oxidation processes (AOPs), pointing out its potential prominent role in the wastewater treatment [3,4]. These treatment processes are considered as very promising methods for the remediation of ground and

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surface waters that are polluted by non-biodegradable, toxic organic industrial effluents. In particular, photocatalysis involving titanium dioxide (TiO_2) seems a promising alternative to be used in rural areas. As a matter of fact, this method has been successfully employed in the treatment of wastewater containing pesticides in laboratory experiments [5,6]. However, as the number and concentration of contaminants increase, the process becomes more complicated and challenging problems such as catalyst deactivation, slow kinetics, low photo efficiency and unpredictable mechanism need to be solved. Despite the great efforts devoted to the study of photocatalytic processes, only few studies have been found in the literature of their application on industrial scale [7]. Although total elimination of the active species can be achieved in most cases, complete mineralization of organic matter usually requires longer periods of treatment. It is clear that TiO_2 alone cannot undertake practical applications of industrial and environmental concentration and for this reason, another alternative treatment which overcomes the major drawbacks of photocatalytic oxidation and offers more advantages is photolytic ozonation process (O_3/UV). This process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals [8]. Since the maximum absorption of ozone molecules is at 253.7 nm, the light source commonly used is a medium pressure mercury lamp wrapped in a quartz sleeve which can generate the UV light at a wavelength of 200–280 nm. The reaction mechanism starts with activating the ozone molecule by UV to form oxygen radical, which then combine with water to form hydroxyl radicals as shown in Eqs. (1) and (2). This radical acts as a primary oxidant in the oxidation process.

$$O_3 + h\nu \rightarrow O_2 + O(1D) \tag{1}$$

$$O(1D) + H_2O \rightarrow 2OH^{\bullet} \tag{2}$$

Ozonation process is greatly influenced by the pH. Depending on the nature of the pollutant and the pH, it may be either molecular ozone attack or radical attack. At higher pH, the formation of hydroxyl radicals and subsequently the radical pathway would be enhanced as long as there are no hydroxyl radical scavengers present in the solution. When such scavengers are present at high concentration they can impede the elimination of pollutants. The presence of bicarbonate and carbonate plays an important role as scavengers of hydroxyl radicals in natural systems. The products of a reaction between hydroxyl radical and carbonate or bicarbonate are passive carbonate or bicarbonate radicals, which do not interact further with ozone or organic compounds.

This paper aims at the comparative study between the photocatalytic oxidation and photolytic ozonation process for the degradation of pesticide. It is important to emphasize that, in practical oxidative degradation, such as those envisaged in industrial water treatment, it is not simply the disappearance of the pollutant but the conversion of all organic carbon into inorganic carbon. As the effluents from pesticide industry are not contaminated just by the pure pesticides, it is more realistic to study the degradation of commercial pesticides. Hence, the present study aimed at the degradation of commercial grade carbendzim, a commonly used pesticide in India, by photocatalytic oxidation and photolytic ozonation processes. The optimization studies were conducted and the degradation of model pesticide carbendazim was evaluated from TOC removal at regular intervals of time. The rate constant and the mineralization achieved in both processes were compared to arrive at a best treatment process for the degradation of the pesticide.

2. Materials and methods

2.1. Chemicals

Carbendazim (50% WP, commercial grade) was used as a model pesticide. TiO_2 (Degussa P25, Germany) was used as photocatalyst without any further preliminary treatment. Other chemicals used in the study viz., KI, $Na_2S_2O_3$ $5H_2O$, H_2SO_4 and NaOH were 98% pure and were supplied by Merck. All the aqueous solutions were prepared with double distilled water.

2.2. Experimental

In this paper, a detailed study on the degradation of carbendazim in acidic medium by photocatalytic oxidation and photolytic ozonation is reported. A batch annular reactor made entirely of pyrex glass with an effective volume of 500 mL and water-jacketed to maintain a solution temperature of 20±1°C was used for all experiments. The schematic reactor set up is shown in Fig. 1. The UV lamp was placed in a double-walled vessel known as an immersion well, which was made up of quartz. Medium pressure mercury lamps were used as UV source (Heraeus Noblelight Inc., Germany, 125 W, UV-C/254 nm). The reactor had an inlet for delivering the reagents and two outlets. The samples were collected from the bottom outlet, and the unutilized O_3 from the reactor after the reaction was collected from the top of the reactor and allowed into buffered KI traps to destroy ozone and then in to fume hood. The whole reactor was mounted on a magnetic stirrer to ensure complete homogeneity of the reacting solution. The reactor was wrapped with aluminium foil to prevent the UV ray penetration into the working area.

The experiments were conducted under pH 3, 6 and 9, ozone dosages 0.12, 0.28, 0.48 and 0.57 g/h, catalyst dosage 0.5, 1, 1.5 and 2 g/L for 1 h duration to arrive at optimized reaction conditions for carbendazim degradation by photocatalytic oxidation and photolytic ozonation. Then, two experimental sets (TiO_2/UV, UV/O_3) were conducted at the optimized reaction conditions to arrive at the best

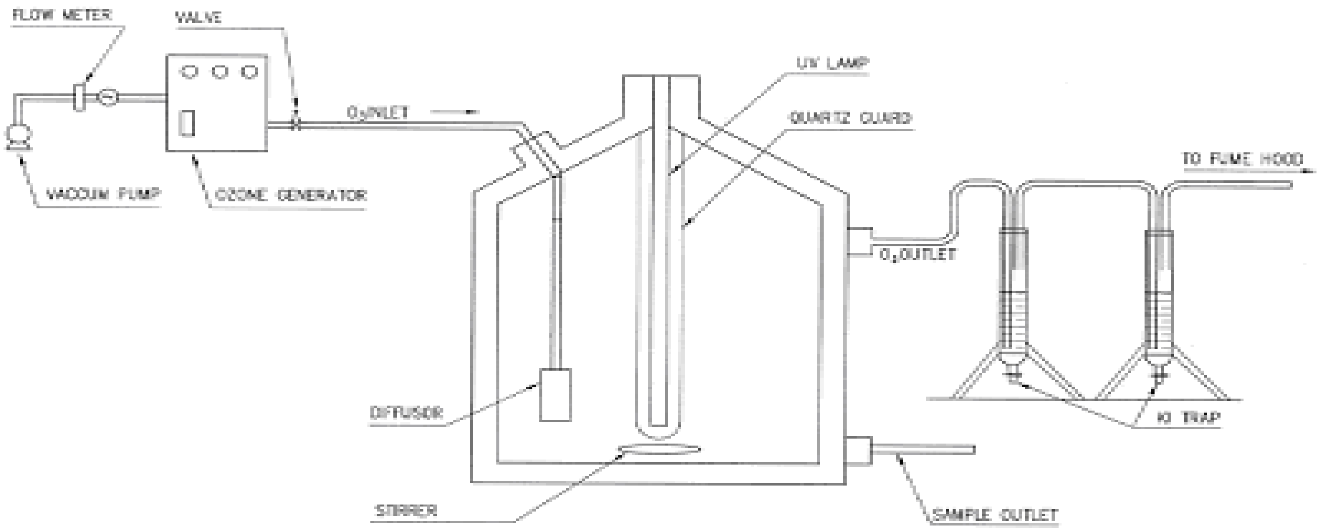

Fig. 1. Experimental setup for photocatalytic oxidation and photolytic ozonation.

treatment process based on the pesticide removal and mineralization. Air generated from the vacuum pump was allowed into the ozone generator (Indiozone, India) to generate ozone gas and the ozone–air mixture was fed through a fine orifice located at the bottom of the reactor filled with 40 mg/L carbendazim solution. The flow rate was adjusted to generate the required ozone dose. The initial pH of the carbendazim solution was 4.6 and was adjusted using 0.1 N H_2SO_4 or 0.1 N NaOH. TiO_2 (Degussa P25) was used as photocatalyst without any further preliminary treatment. The temperature of the suspension was maintained at 20±1°C. The slurry containing the catalyst and carbendazim was mixed by magnetic stirrer and allowed to attain steady state in the dark for 30 min after which it was exposed to UV light source. Aliquots of samples were withdrawn at specified intervals of time and the photocatalyst was immediately filtered by centrifugation. The decrease in concentration of carbendazim during the degradation was quantitatively measured by HPLC with a C18 column (4 mm id and 250 mm length) at room temperature (27°C) containing the packed material of Erosphen-100 of 5 μm size. The mobile phase used was acetonitrile and triple distilled water (60:40 v/v). The amount of ozone generated was determined by iodometry [9]. Minerlisation achieved during the process was measured using total organic carbon analyser (Shimdazu, Japan).

3. Results and discussion

3.1. Photocatalytic oxidation

3.1.1. Effect of pH

The pH of the solution is an important variable in the evaluation of aqueous phase mediated photocatalytic reactions since it affects the adsorption and dissociation of the substrate, catalyst surface charge, oxidation potential of the valence band and other physicochemical properties of the system [10]. The role of pH on the photocatalytic degradation was studied in the pH range 3–9 with 40 mg/L carbendazim and 1 g/L TiO_2. Fig. 2 shows the TOC removal achieved at different initial pH values, and the maximum TOC removal achieved in 1 h was 44.4% at pH 4. Pelizzetti and Schiavello [11] reported that acid base property of the metal oxide surface has considerable implications in their photocatalytic activity and this has been reviewed by Bahnemann [12]. In the present investigation the TOC removal obtained in the pH range 4–8 is in accordance with pHzpc of TiO_2 (pHzpc of TiO_2 = 6.9). pH 3 is less than pKa of carbendazim which

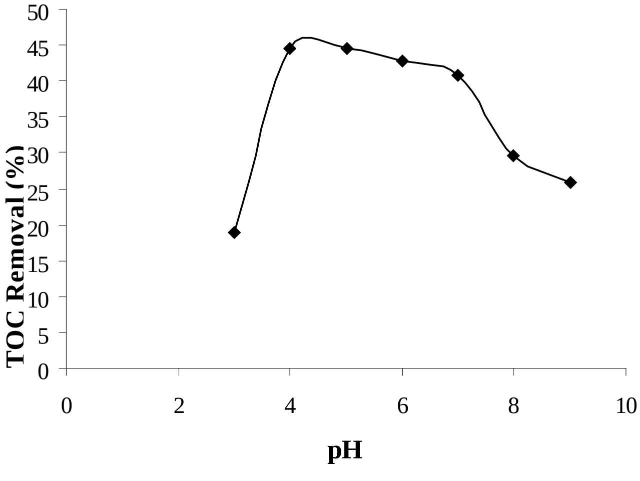

Fig. 2. Effect of pH in photocatalytic oxidation of carbendazim wastewater.

is 4.5 in aqueous solution, where the protonation takes place and the protonated products are more stable under UV radiation than its main structure. On the other hand, due to the zero point charge of TiO_2 the catalyst surface is also positively charged leading to a lower level of TOC removal at pH 3. At pH 4, on the other hand, there will be significantly higher molecules in their non-protonated form, providing a higher level of adsorption into catalyst surface favouring higher TOC removal.

3.1.2. *Effect of catalyst dosage*

Experiments were carried out to assess the optimum catalyst dosage by varying the amount of TiO_2 from 0 to 2 g/L at pH 4 with 40 mg/L carbendazim. The TOC removal achieved with respect to TiO_2 dosage is depicted in Fig. 3. The results showed that the TOC removal increased with the increase in TiO_2 dosage up to 1 g/L after which a decrease was observed. Maximum TOC removal achieved in 1 h was 46.4% with 1 g/L of TiO_2. The initial increase in TOC removal with the increase in dosage was due to the increase in the number of active sites, which in turn increased the hydroxyl radical generation due to the increase in the surface area and light absorption. The decrease above 1 g/L was attributed due to scattering of light by the increased opacity of the suspension and the decrease in the number of active sites [13]. The increased loading of catalyst increased the quantity of photons absorbed and consequently the degradation increased. Further increase in the catalyst dosage above the optimum level resulted in the decrease in light penetration and deactivation of activated molecules due to collision with the ground state molecules [14].

3.2. *Photolytic ozonation*

3.2.1. *Effect of pH*

To study the effect of pH on photolytic ozonation, the reaction was performed at different initial pHs ranging from 3 to 9 with 40 mg/L carbendazim. Generally, O_3 reacts with organic compounds in water directly via a molecular O_3 pathway or indirectly via a radical pathway [15]. One of the major generation sources of these radicals is the self-decomposition reaction of ozone which is accelerated by the action of hydroxyl ions [16]. At higher pH, the formation of hydroxyl radicals and subsequently the radical pathway would be enhanced as long as there are no hydroxyl radical scavengers present in the solution. When such scavengers are present at high concentration they can impede the elimination of pollutants. Here, under the experimental conditions used, the TOC removal increased with the increase in pH, and the results in Fig. 4 indicate that maximum of 63.3% removal was achieved at pH 9 in 1 h indicating indirectly the radical pathway of the photolytic ozonation. At low pH, the generation of hydroxyl radicals is less resulting in lower removal and as pH increases, the amount of hydroxyl radical increases and hence the removal. Similar results were also reported by Andreozzi et al. [17] when paraquat was ozonated. It was found to be reactive with ozone at pH values above 5, where radical reaction pathway started to be a significant factor. Yao and Haag [18] reported a slow conversion of simazine at pH 2, and improved conversion was reported by Lai et al. [19] at high pH.

3.2.2. *Effect of ozone dosage*

To study the effect of the influent ozone dosage, ozonation was carried out at different ozone dosages applied ranging from 0.12 g/h to 0.57 g/h with 40 mg/L carbendazim at pH 9. The results in Fig. 5 indicated that the TOC removal increased with the increase in the dosage from 0.12 g/h to 0.44 g/h, above which a decrease was observed. At 0.44 g/h O_3 dosage, 62.5% TOC removal was observed in 1 h. The increase in TOC removal with the

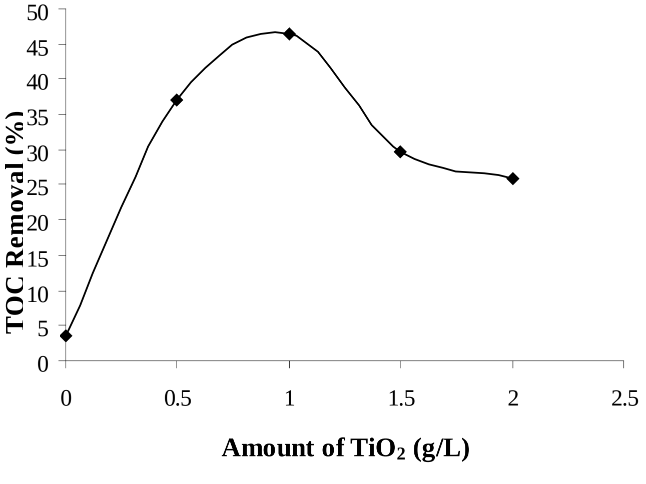

Fig. 3. Effect of TiO_2 dosage in photocatalytic oxidation of carbendazim wastewater.

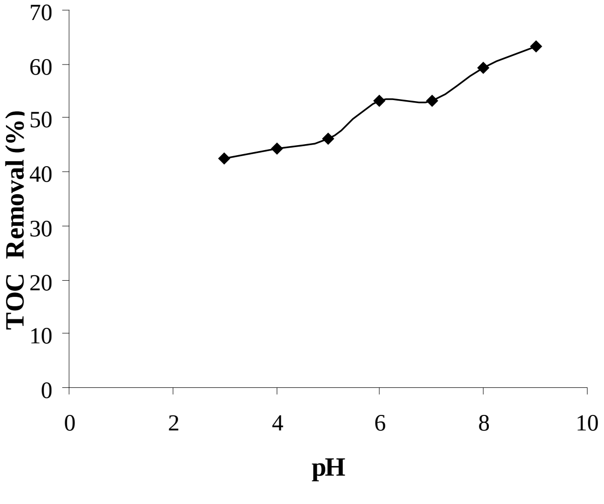

Fig. 4. Effect of pH in photolytic ozonation of carbendazim wastewater.

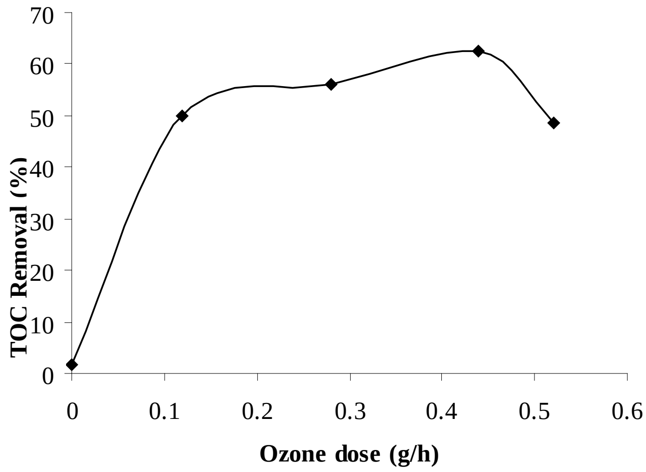

Fig. 5. Effect of ozone dosage in photolytic ozonation of carbendazim wastewater.

increase in the ozone dosage could be attributed to the fast reaction of ozone with the reactant molecules. At a high dosage, the number of ozone molecules was already high enough for the reactant and due to less contact time of ozone with the reactant a decrease in TOC removal was observed [20]. Similar results were also reported for the degradation of 4-chloro-2 methylphenoxy acetic acid [21] and in the DMSO degradation [22].

3.3. Comparison of photocatalytic oxidation and photolytic ozonation

The main influencing parameters in photocatalytic oxidation and photolytic ozonation were optimized by the above preliminary studies after which experiments were conducted at the optimized reaction conditions with 40 mg/L carbendazim to asses the kinetics of the processes. The photolytic ozonation reactions were carried out at pH 9 with a constant ozone dosage of 0.48 g/h, and photocatalytic oxidation was performed with 1 g/L TiO_2 at pH 4. Experiments were also performed in the absence of UV light. Dark adsorption studies with the catalyst alone revealed negligible degradation. A plot of ln $(TOC_o)/(TOC)$ vs. time showed that the reaction followed pseudo first order kinetics and gave straight lines of slope k. The pseudo first order rate constant for the above reactions and the mineralization achieved in 3 h is listed in Table 1. The results revealed that photolytic ozonation improved the degradation rate due to increased production of hydroxyl radicals and it was 2 times highly efficient than the photocatalytic oxidation process and 1.6 times than ordinary ozonation. Correlation coefficient > 0.98 in all cases confirmed the goodness of the assumed kinetics for the ozonation and photocatalytic experiments. TOC decreased from 25.8 mg/L to 3.6 mg/L with the decrease in concentration from 40 mg/L to 1.5 mg/L by the photolytic ozonation process. Fig. 6 shows the amount of carbendazim removed by both these processes under the optimized reaction conditions. Studies on these two processes at optimized conditions based on pesticide removal and mineralization showed that photolytic ozonation is highly efficient compared to photocatalytic oxidation process.

Table 1
Kinetic rate constants of photocatalytic oxidation and photolytic ozonation process

S. No.	Process	k (min^{-1})	R^2	Mineralization (%)
1	O_3	0.0131	0.9842	72.6
2	O_3/UV	0.0212	0.9638	85.4
3	TiO_2/UV	0.0103	0.9784	62.2

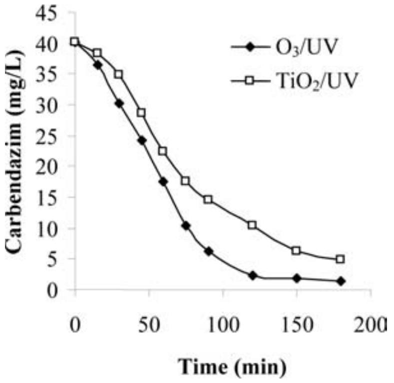

Fig. 6. Removal of carbendazim by photocatalytic oxidation and photolytic ozonation.

4. Conclusion

Treatment of pesticide industry effluents is mandatory to mitigate environmental and health risks. Recent advances in chemical oxidation techniques can be utilized for recycling of industrial wastewater and some active ingredients in the pesticide industry. This study has investigated two simple chemical oxidation processes for the removal of carbendazim as a model pesticide. The rate constant and the mineralization achieved in both processes revealed that photolytic ozonation performed better than photocatalytic oxidation. Further, this process does not encounter the problems faced in the photocatalytic oxidation such as either the removal or reuse of the TiO_2 or coating of the catalyst on inert surfaces. It also facilitates easy transfer of technology to industrial scale applications and hence can be a potential treatment method for non-biodegradable recalcitrant organic pollutants such as pesticides.

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