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A study on degradation of pesticide wastewater by TIO_2 photocatalysis

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Photocatalytic degradation of Carbendazim, a commercial grade pesticide, has been investigated. Optimum degradation (76%) of Carbendazim (40 mg/l) was observed in 60 min at pH 6 and catalyst concentration (1g/l). Degradation was lowered by the presence of carbonate and phosphate ions. Studies on real industrial wastewater revealed that removal of pesticide (99%) was faster and mineralization (76%) required longer duration. Formation of inorganic ions (ammonium and nitrate) proved fragmentation of pesticide and formation of intermediates.

Keywords: Carbendazim, Industrial wastewater, Mineralization, TiO_2 photocatalysis

Introduction

Effluent discharge from pesticide manufacturing or formulating industries and agricultural run off are major sources of pesticides in environment[1] and these pesticide industry wastewaters pose a high threat for aquatic systems. Compared with direct chemical oxidation, advanced Oxidation Processes (AOPs), in which hydroxyl radical (OH^-) is produced by means of chemical, photochemical, photocatalytic or electrochemical reactions[2], are more effective for treatment of wastewaters containing highly recalcitrant organic pollutants. Photocatalytic oxidation processes are included within this group of AOPs and is extensively studied and developed to degrade various organic compounds and pollutants in water[3-5]. Photocatalytic processes make use of various oxides (TiO_2, ZnO, ZrO_2, CeO_2 etc.) or sulphides of CdS, ZnS etc as photocatalyst[6-9]. Surface area and number of active sites offered by catalyst for adsorption of pollutant plays an important role in deciding overall rates of degradation. Among many catalysts, TiO_2 in anatase form seems to have the most interesting attributes[4,10] (high stability, good performance and low cost). Further, its photocatalytic activity can be enhanced by pretreatment with sulphuric acid or by doping with platinum[11,12]. In India, formulation grade pesticides are directly applied to fields and major part of pesticide industries are formulating units. Only very limited studies has been published with formulation grade pesticides.

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This study investigates feasibility of photocatalytic degradation of commercial grade pesticide Carbendazim using TiO_2 suspension and influence of different parameters (pH, catalyst dosage, Carbendazim concentration, inorganic ions in wastewater and contact time of reaction).

Materials and Methods

Chemicals

Commercial grade Carbendazim (50% WP) was obtained from pesticide dealers in Chennai, India. Double distilled water was employed to make stock solution. Commercially available TiO_2 (Degussa P-25; anatase, 70%; rutile, 30%; surface area, 50 $m^2 g^{-1}$; particle size, 25 nm), obtained from Degussa, Germany, was used as photocatalyst. Other chemicals (NaOH and H_2SO_4), used for adjusting pH and inorganic salts, were obtained from Merck.

Experimental Procedure and Analysis

A batch annular reactor (500 ml), water-jacketed to maintain a solution temperature (19±1°C), was used for all experiments (Fig. 1), consisting of following three parts: i) outside Pyrex glass; ii) Pyrex glass thimble, of which head part is fitted to outside container to form a gastight seal and running water is passed through thimble to cool reaction solution; and iii) empty quartz chamber, in which a mercury lamp (PHILIPS, 125W, 254 nm) is immersed. TiO_2 powders were suspended between thimble and outside container using a magnetic stirrer. Reactor was wrapped with aluminium foil

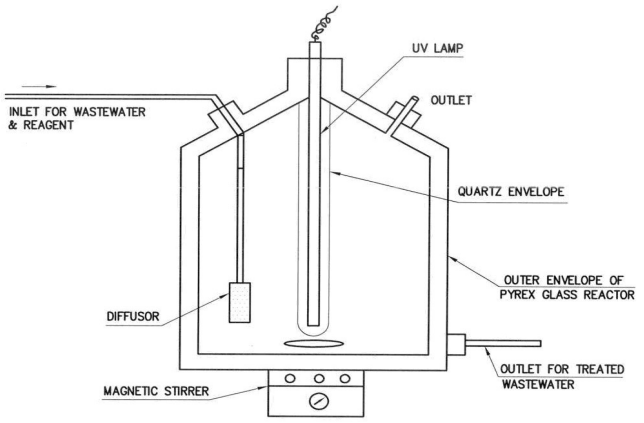

Fig. 1—Experimental setup-photocatalytic reactor

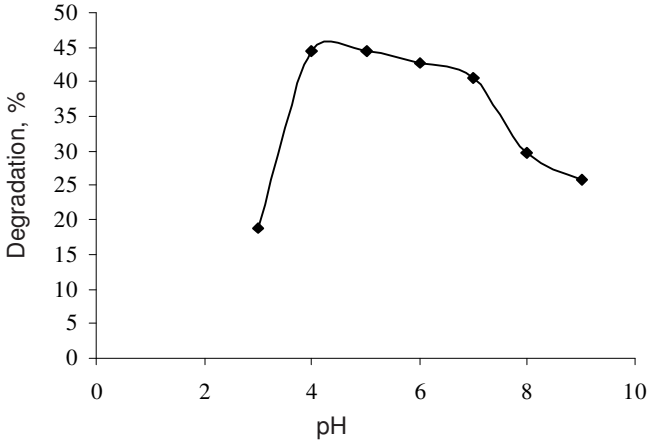

Fig. 2—Effect of pH on TiO_2 photocatalysis (Carbendazim, 40 mg/l; TiO_2, 1 g/l; pH, 3-9)

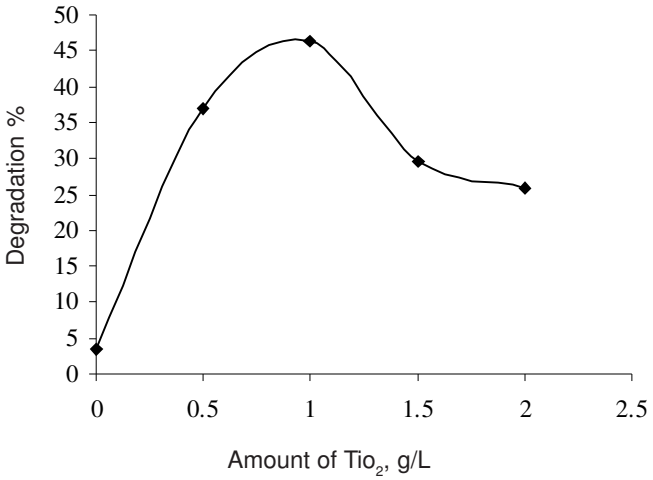

Fig. 3—Effect of catalyst concentration on TiO_2 photocatalysis(Carbendazim, 40 mg/l; TiO_2, 0-2 g/l; pH, 6)

to prevent UV ray penetration into working area. Desired concentration of Carbendazim wastewater was prepared by dissolving pesticide in water after adjusting pH using H_2SO_4 or NaOH. Required amounts of TiO_2 was added and stirred for 30 min in dark to attain equilibrium and then transferred to reactor. Aliquots were withdrawn at specific time intervals and analyzed after centrifugation followed by filtration to remove titania particles.

UV-Vis spectrophotometer (Spikol 1200) was used to measure absorbance spectra of Carbendazim, which showed characteristic absorbance maxima at 285 nm in UV region. Concentration of Carbendazim was measured from calibration graph obtained with standard pesticide. Presence of pesticide was also monitored with HPLC analysis. Chemical oxygen demand (COD) was measured by open-reflux potassium dichromate titrimetric method[13]. Residual total organic carbon (TOC) was measured using TOC analyzer. Ammonium ions and nitrate ions were identified as per standard procedure[13].

Results and Discussion

Effect of pH

Role of pH[14] on photocatalytic degradation was studied in pH range 3-9 with Carbendazim (40 mg/l) and TiO_2 (1 g/l) keeping all other experimental conditions constant (Fig. 2). Maximum degradation (44.4%) was achieved in 1 h at pH 4. Degradation obtained in pH range 4-8 is in accordance with pH_{zpc} of TiO_2. At pH 4, there will be significantly higher molecules in non-protonated form, providing higher level of adsorption into catalyst surface favouring degradation. As difference between degradation at pH 4 and under its natural pH 6.73 after 60 min amounts to only 6%, natural pH was chosen as a moderate and optimum pH value and experiments were followed under this pH.

Effect of TiO_2 Dosage

A series of experiments were carried out to assess optimum catalyst dosage by varying amount of TiO_2 (0-2 g/l) at pH 6 with Carbendazim (40 mg/l). Degradation increased with increase in TiO_2 dosage up to 1 g/l, after which a decrease was observed (Fig. 3). Maximum degradation (46.4%) was achieved with 1 g/l of TiO_2 in Carbendazim wastewater. Initial increase in degradation with increase in dosage was due to increase in number of active sites, which in turn increased hydroxyl radical generation due to increase in surface area and light absorption. Decrease above 1 g/l was attributed due to scattering of light by increased opacity

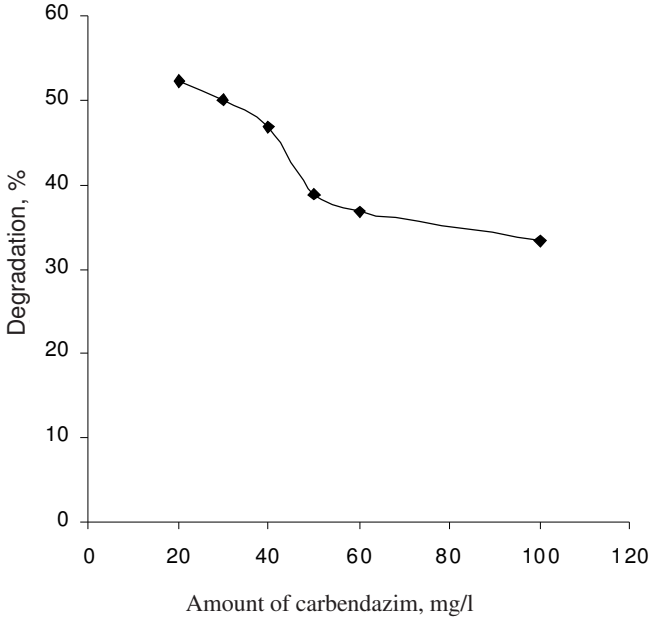

Fig. 4—Effect of initial concentration on TiO_2 photocatalysis(Carbendazim, 20-100 mg/l; TiO_2, 1 g/l; pH, 6)

Table 1—Pseudo First Order rate constant values at different initial concentration of pesticide

S No.	Concentration of Carbendazim, mg/l	K, min^{-1}	R^2
1	20	0.0129	0.9558
2	30	0.0121	0.9692
3	40	0.0112	0.9709
4	50	0.0087	0.9254
5	60	0.0082	0.9490
6	100	0.0074	0.8873

of suspension and decrease in number of active sites[15]. In other words, increase in catalyst dosage above optimum level resulted in decrease in light penetration and deactivation of activated molecules due to collision with the ground state molecules[16] and aggregation of particles may also reduce effective surface area of catalyst for adsorption of reactant[17].

Effect of Initial Concentration

In order to study effectiveness of photocatalysis with increasing pollutant concentration, experiments were conducted by varying amount of Carbendazim (20-100 mg/l) with TiO_2 (1 g/l) at pH 6. Degradation decreased marginally with increase in initial concentration of pesticides up to 60 mg/l, above which there was drastic

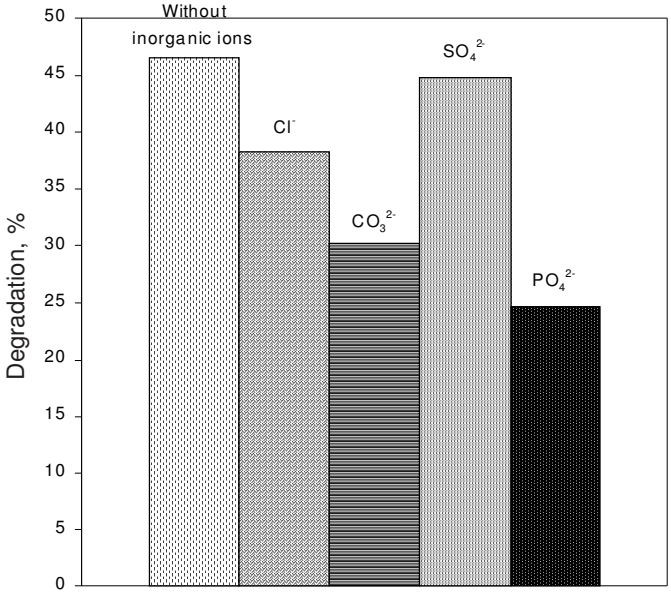

Fig. 5—Effect of inorganic ions on TiO_2 photocatalysis(Carbendazim, 40 mg/l; TiO_2, 1 g/l; pH, 6)

decrease (Fig. 4). Degradation reduced from 52% with 20 mg/l to 33% with 100 mg/l of Carbendazim. At lower concentration, hydroxyl radicals were sufficient to attack pesticide molecules. But with increase in concentration, catalyst surface available to generate hydroxyl radical was not sufficient enough to attack pesticide molecules, thereby decreasing degradation. When initial concentration exceeded optimum level, degradation decreased. Moreover, as initial pesticide concentration increased, path length of photons entering solution decreased and at low concentration, number of photon absorption by catalyst increased[18]. Hence, rate of degradation is proportional to substrate concentration in accordance with apparent Pseudo First Order kinetics[19] (Table 1). Since illumination time and amount of catalyst are constant, radicals formed on TiO_2 remain constant. Hence, relative number of hydroxyl and O^{2-} species attacking pesticide molecules decreased with increase of pesticide concentration[20]. At high initial concentration, absorption of UV light by pesticides was higher than catalyst since active sites are blocked by pesticide molecules. Such screening effect had been observed in other photocatalytic degradation processes also[16, 21].

Effect of Inorganic Ions

Influence of inorganic ions was studied by adding TiO_2 (1 g/l), Carbendazim wastewater (40 mg/l) at pH 6 and degradation was reduced as follows: chloride (Cl^-),

Table 2—Photocatalytic degradation of real industrial wastewater

S No.	Time min	Concentration mg/l	Mineralization efficiency %	Ammonium ions mg/l	Nitrate ions mg/l
1	0	21.4	0	0	0
2	60	18.2	7.4	0	0
3	120	14.5	15.9	0.06	0
4	180	0.50	43.8	0.24	0.04
5	240	0.23	60.9	1.40	0.18
6	300	0.10	68.3	4.20	0.34
7	360	0.05	76.5	5.80	1.60

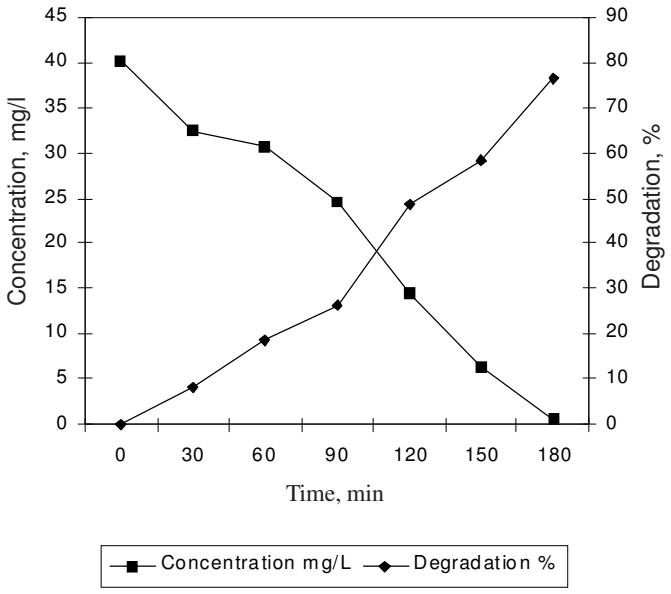

Fig. 6—Effect of contact time on photocatalysis(Carbendazim, 40 mg/l; TiO_2, 1 g/l; pH, 6)

8.4; carbonate (CO_3^{2-}), 16.4; sulphate (SO_4^{2-}), 1.8; phosphate (PO_4^{3-}), 22%; (Fig. 5).

Effect of Contact Time

Experiments conducted for 3 h at optimum conditions (Carbendazim wastewater, 40 mg/l; pH, 6; TiO_2, 1 g/l) indicated that pesticide removal increased with increasing irradiation time along with increase in degradation (Fig. 6). Light induced degradation proceeded slowly after 1 h irradiation, might be due to stable intermediates formed, which compete with parent molecules in degradation process. Concentration of pesticide was reduced (99%) with COD removal (76.5%) in 3 h. Slow degradation of dye after certain time limit is reported[22] due to difficulty in converting nitrogen atoms of dye into oxidized nitrogen compounds.

Studies with Industrial Wastewater

To asses applicability of TiO_2 photocatalysis, studies were conducted with pesticide industry wastewater with other optimum conditions. Decrease in concentration of Carbendazim in wastewater and TOC removal was monitored at different time intervals at pH 6. TOC mineralization proceeds comparatively slower than removal of pesticide, might be due to formation of stable intermediates and presence of larger amount of organic matter in industrial effluent (Table 2). Fragmentation of pesticide structure was confirmed by increase in TOC removal and formation of inorganic ions.

Conclusions

Pesticide wastewater degradation revealed 99% removal of active ingredient of pesticide and 76% mineralization using photocatalytic method. Complete mineralization could be achieved by further increasing reaction time or by adding some additives, which would speed up reaction. Based on optimization studies performed with simulated wastewater containing pesticide and real industrial wastewater, photocatalysis could be promoted as feasible technology in industries and can be really competitive with conventional methods.

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