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PHOTO DEGRADATION STUDIES ON ZIRAM USING HOMOGENEOUS AND HETEROGENEOUS PHOTOCATALYST

K. Ramadevi and S. K. Shivaranjani
Department of Civil Engineering, Kumaraguru College of Technology, Coimbatore, India
E-Mail: ramadharans@gmail.com

ABSTRACT

Photocatalytic degradation of Ziram was performed on wastewater by various photodegradation techniques via Solar, Solar/TiO_2, UV and UV/TiO_2processes. Studies were also performed to optimize the operating parameters such as pH, initial concentration, catalyst dosage and contact time. It was found that the UV/TiO_2 photo catalytic process was more effective than any other methods studied for degradation of the Ziram. The maximum degradation of Ziramwas 92.7% at 300 minutes for initial pH 5, initial Ziram concentration of 20mg/l and TiO_2 dosage of 1 g/l. The kinetic constant (k) for UV/TiO_2 was found to 9.62 times greater than solar/TiO_2 process and 8.19 times greater than the UV process. The order of reaction rate constant was UV/TiO_2>UV > Solar/TiO_2> Solar.

Keywords: ziram, solar, photocatalyst, UV, UV/ TiO_2.

1. INTRODUCTION

Effluent discharge from pesticide manufacturing or formulating industries and agricultural runoff are major sources of pesticides in environment and this pesticide industry wastewater pose a high treat for aquatic system. 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, are more effective for treatment of wastewater containing highly recalcitrant organic pollutants. As the ziram causes more adverse effect, not only to the environment but also to the human beings, hence it is necessary to degrade such a compound by any of the treatment method. There are many cases of illness and death related to ziramexposure source. It has been demonstrated that aqueous solutions of several herbicides can be completely oxidized by photocatalytic processes, in which photo induced holes in semiconductor particles oxidize hydroxide ions or water molecules adsorbed on the surface of the particles to produce •OH and $•O_2^-$ radicals which subsequently attack adsorbed organic molecules. The scope of the present study is to identify the best AOP for the degradation of pesticides in wastewater. Among many catalysts, TiO_2 in anatase form seems to have the more interesting attribute (High stability, good performance and low cost). Among AOP, Photocatalysis is an attractive method to degrade ziramfrom pesticide wastewater. The main advantage of Photocatalysis process is that they do not create any sludge during its operation compared to other treatment methods namely lime softening, powder activated carbon, ozonation, ion-exchange, membrane filtration technologies such as reverse osmosis and nanofiltration

2. MATERIALS AND METHODS

Commercial grade Ziram (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; particle size, 25nm), 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

3. EXPERIMENTAL PROCEDURE

A batch annular reactor (500 ml) , water -jacketed to maintain a solution temperature (19 ± 1ºC) , was used for conducting experiments , 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, 254nm) is immersed. TiO_2 powders were suspended between thimble and outside container using a magnetic stirrer. Reactor was wrapped with aluminum foil to prevent UV ray penetration into working area. Desired concentration of Ziram 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.

Experiments were conducted in batch mode in 2 L glass vessel containing 500 ml of ziram solution. The solution was mixed with magnetic stirrer to ensure complete mixing of the reagent (TiO_2). Samples were

collected at regular intervals for a period of 3 h for analysis.

UV-Vis spectrophotometer (Spikol 1200) was used to measure absorbance spectra of ziram, which showed characteristic absorbance maxima at 450nm in UV region. Concentration of ziram was measured from calibration graph obtained with standard pesticide.

4. RESULTS AND DISCUSSIONS

A. Effect of pH

Role of pH on photocatalytic degradation was studied in pH range 4 - 8 with Ziram (100 mg/l) and TiO_2 (1g/l) keeping all other conditions constant. Maximum degradation (54.82 %) was achieved in 3 hrs at pH 5. Degradation obtained in pH range 4-8 is in accordance with pH_{zpc} of TiO_2. At pH 5, there will be significantly higher molecules in non - protonated form, providing higher level of adsorption into catalyst surface favoring degradation.

The degradation is higher in UV/TiO_2 process than the other processes. The effect of pH in Solar, Solar/TiO_2, UV and UV/TiO_2 is shown in Figure-1.

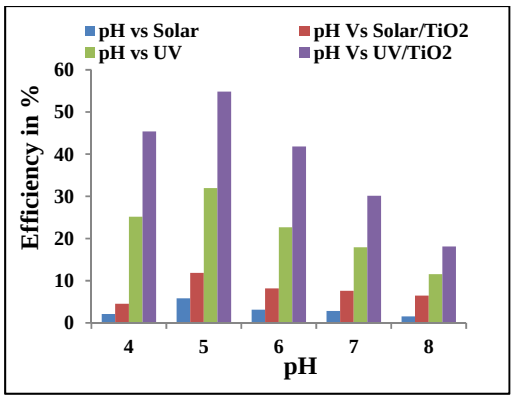

Figure-1. Effect of pH.

B. Effect of initial concentration

In order to study the effect of initial concentration of aqueous Ziram on photo degradation by various solar & UV methods, the experiments were performed in the concentration range of 20 - 100mg/l by maintaining other parameters such as pH 5, TiO_2 dosage: 1g/*l* and contact time of 180 minutes and the results were obtained.When initial concentration exceeded optimum level, degradation decreased. Hence, relative number of hydroxyl and oxygen species attacking pesticide molecules decreased with increase of pesticide concentration. But with increase in concentration, catalyst surface available to generate hydroxyl radical was not sufficient enough to attack pesticide molecules, thereby decreasing degradation.

Moreover, as initial pesticide concentration increased, path length of photons entering solution decreased and at low concentration, number of photon absorption by catalyst increased at high initial concentration, absorption of UV light by pesticide was higher than catalyst since active sites are blocked by pesticide molecules.

The effect of initial concentration in Solar, Solar/TiO_2, UV and UV/TiO_2 is shown in Figure-2.

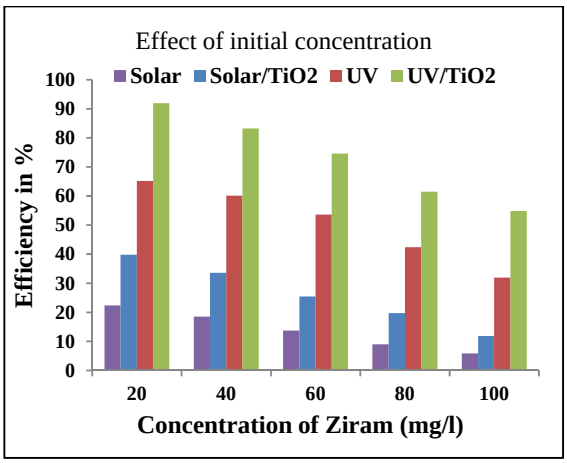

Figure-2. Effect of initial concentration (mg/l).

C. Effect of catalyst dosage

A series of experiments were carried out to assess optimum catalyst dosage by varying amount of TiO_2 (0.5 - 2.5 g/l) at pH 5 with ziram (20 mg/l). Degradation increased with increase in TiO_2 dosage up to 1 g/l, after which a decrease was observed (Figure-3). Maximum degradation (91.95 %) was achieved with 1 g/l of TiO_2 in ziram wastewater. The catalyst concentration required for particular pollutant is to be optimized as the excess catalyst may reduce the amount of photo energy being transferred in the medium due to opacity offered by the catalyst particles. Decreasing above 1g/l was attributed due to scattering of light by increased opacity of suspension, decrease in number of active sites and deactivation of activated molecules due to collision with the ground state molecules and aggregation of particles may also reduce effective surface area of catalyst for adsorption of reactant.

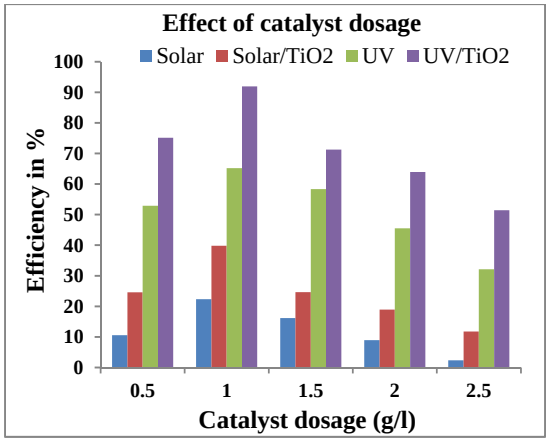

Figure-3. Effect of catalyst dosage.

D. Effect of contact time

Experiments conducted for 3 hrs at optimum conditions (Ziram wastewater, 20mg/l; pH 5; TiO_2 1g/l) indicated that pesticide removal increased with increasing irradiation time along with increase in degradation (Figure 4). Light induced degradation proceeded slowly after 1 h irradiation, might be due to stable intermediates formed, which compete with parent molecules in degradation process. Slow degradation of wastewater after certain time limit is reported due to difficulty in converting nitrogen atoms of wastewater into oxidized nitrogen compounds.

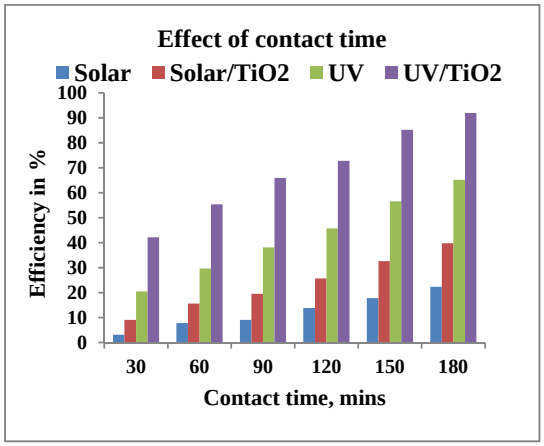

Figure-4. Effect of contact time.

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