Photocatalytic Degradation of Simulated Monocrotophos Waste Water using Synthesized Zinc Oxide Nanocatalyst under UV Radiation

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Abstract **- Monocrotophos is an organophosphorous pesticide most commonly in India. The ZnO nano catalyst is prepared in laboratory by Sol-Gel method. The degradation rate of simulated monocrotophos waste water is studied under UV light souce by varying pH, Catalyst dosage, Contact Time and Initial Concentration. The maximum removal efficiency of 74% is achieved by UV/ZnO processes. IUPAC name of monocrotophos is Dimethyl (E)-1-methyl-2-(methylcarbamoyl) vinyl phosphate.**

Keywords: Advanced Oxidation, Sol-Gel, Monocrotophos, Nano ZnO, Photocatalysis.

1. INTRODUCTION

Water is an essential element for human life. It covers 71% of the Earth's surface. As the population of planet continues to increase, a larger supply of water is required for drinking, agricultural use and other needs. Agriculture plays a dominant role in Indian economy and more than 80% of population depends on it. Modern agricultural practices relied heavily on large scale use of fertilizers and pesticides to increase crop yield. This results in increased levels of pesticides in the environment. Use of chemical pesticides in India was made for the first time in 1948 on a small-scale by importing Dichlorodiphenyl Trichloroethane (DDT) for malaria control and Benzene Hexachloride (BHC) for locust control (COINDS 1993-94). Pesticides are defined as artificially synthesized substances that are used to fight pests and improve agricultural production. Pesticides are mainly classified under three categories as herbicide, insecticides, fungicides. These are defined as the chemicals used to destroy any insect, fungus, bacterium, virus or rodent, or to attack, repel, sterilize any pest, or to act as a plant growth regulator, defiant, desiccant, etc., Because of their persistence and potential adverse health effects, presence of pesticides in aquatic systems has been recognized as a major issue in many countries. Over dosage of pesticides in aquatic streams affects fish life. Potential of food production is said to be lost in India due to insect pest, plant pathogens, weeds, rodents, birds and by storage.

Monocrotophos ((3-hydroxy-*N*-methyl-*cis*-crotonamide) dimethyl phosphate) is widely used to control aphids, leaf hoppers, mites and other foliage pests. It has been classified as extremely hazardous, with an LD_{50} value of 20 mg kg^{-1} for mammals. The half-life of monocrotophos in soil was reported to be 40–60 days. Monocrotophos is most popular and broadly used organophosphate Pesticide owing to its low cost and high efficiency in controlling pests mainly on cotton crop, rice and sugarcane, and active against heavy diversity of insects in India. IUPAC name of monocrotophos is Dimethyl (E)-1-methyl-2-(methylcarbamoyl) vinyl phosphate. One of the mostly (top 5) used pesticides in INDIA. The molecular structure of Monocrotophos is shown in the Figure 1.

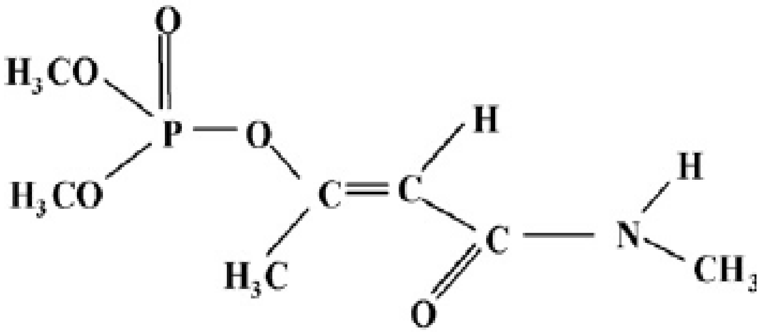

Figure 1. Molecular structure of Monocrotophos

The main objectives of the studies is to synthesize ZnO nano photocatalyst and to characterize the catalyst for particle size (XRD), morphology (SEM), band gap (UV-DRS) and elemental composition (EDS). Experiment is to optimize the various operating parameters namely pH, pollutant concentration, dosage, catalyst dosage, catalyst reuse and contact time.

2. MATERIALS AND METHODS

2.1Chemicals Required

Monocrotophos 36% SL, Zinc sulfate heptahydrate, Diethylene glycol, Ethanol , Potassium dichromate, Hydrogen peroxide, Mercuric sulphate, Ferroin indicator, Sulfuric acid and other chemicals are required.

2.2. Preparation of ZnO nano catalyst

ZnO nanoparticles were synthesized by sol gel method according to the following procedure. 0.015 mol $ZnSO_4.7H_2O$ and 1.2 g diethylene glycol were added to mixed solution of 10 ml ethanol and 300 ml distilled water. The mixed solution stirred with a magnetic stirrer at 85° C for 2 hours to obtain the gel. The obtained gel was dried at 220°C for 1 hour then grounded into fine particles. The temperature of the dried precursor powder was increased at the rate of 1°C/min to attain the required temperature and then allowed the sample to stay at 500°C for 3 hours to obtain the final product (i.e., ZnO nanoparticles).

2.3. Experimental Setup and Procedure

A batch annular reactor made entirely of borosilicate with an effective volume of 500 mL was used for all laboratory scale experiments are illustrated in Figure 2. The UV lamp was placed in a double walled vessel known as immersion well. The tube was inserted at the one side of the quartz cylinder and connected to the bottom of a glass condenser. The other end of the condenser was connected to another side of the quartz cylinder through another tube. The condenser was cooled by cooler in order to prevent the excess heat generated. The reactor was filled with simulated Monocrotophos sample, catalyst and oxidant. The solution was kept under UV lamp of 32 W with continuous stirring using magnetic stirrer for the required period. An aliquot of 5 mL was taken from the reactor at 10 min interval of time. The experiment was carried out for contact time of 0-150 min. The sample was filtered in order to remove the catalyst. The separated catalyst was reused for further runs. Finally, the filtered sample was analyzed for optical density using UV-Visible spectrophotometer at 490 nm as well as for COD estimation.

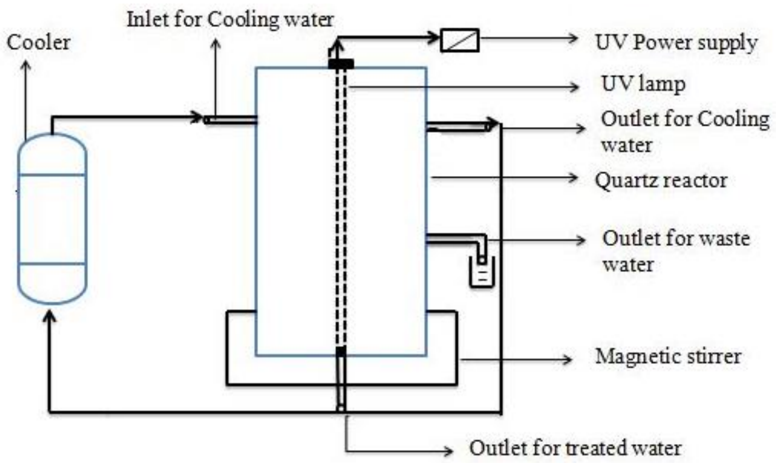

Figure 2. Schematic Diagram of the Experimental setup

3. RESULTS AND DISCUSSION

As part of the study, in this article it is discussed the Effect of pH, Effect of catalyst dosage, Effect of Contact time and Effect of initial pollution concentration to evaluate degradation of monocrotophos.

3.1. Effect of pH

The pH of solution may influence the surface properties of catalyst, charge of the pollutants, generation of free radicals, oxidation potential of the valence band and other physicochemical properties of the system. Therefore, the study of pH influence on the photocatalytic process would be helpful to understand the mechanism of the process as well as for a higher degree of removal (Augustine Chioma Affam and Malay Chaudhuri, *2013*). The role of pH on the rate of photocatalytic degradation was studied in four pH ranges of 3.5, 5.5, 8.5 and 11 with Simulated Waste Water having 0.27 g/L (0.2ml) of Monocrotophos and 1 g/L of nano ZnO keeping all other experimental conditions constant. The photo degradation of monocrotophos at pH ranges of 3, 5.5, 8.5 and 11 reaches up to 41%, 45%, 58% and 50% respectively in UV/ZnO process. Degradation rate increased in alkaline condition because of large amount of OH^- ions are adsorbed on the catalyst surface and removed as a precipitate at pH 8.5. Decrease in degradation rate after pH 8.5 because more pesticide molecules adsorbed on the surface of the catalyst and thus reduce the passage of UV radiation. The effect of pH on ZnO photocatalysis is shown in Figure 3.1

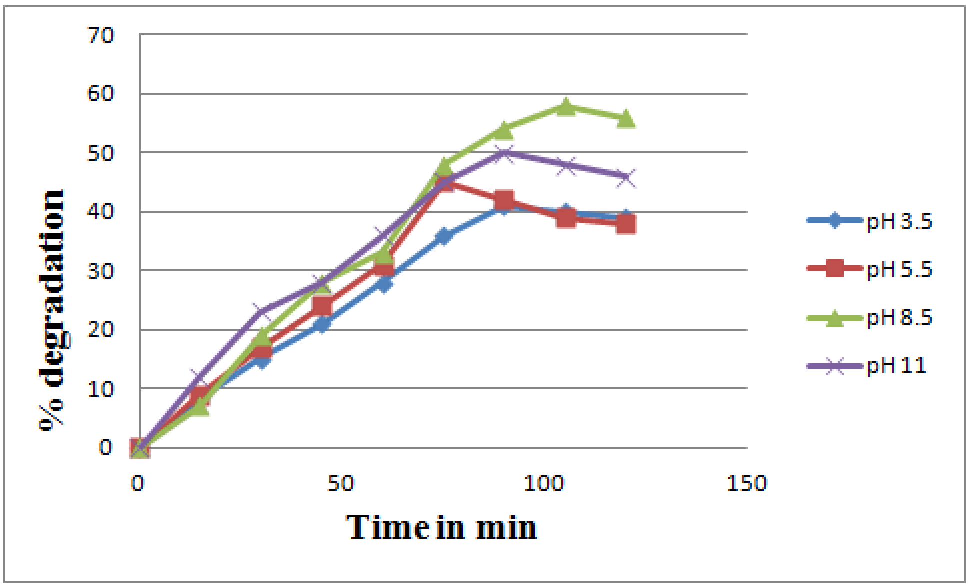

Figure 3.1 Effect of pH on ZnO photocatalysis

3.2. Effect of Catalyst dosage

An adequate amount of the photocatalyst raises the formation of electron, hole pairs to improve the photocatalytic degradation. A series of experiments were carried out to assess the optimum catalyst dosage by varying the amount of ZnO from 0.2 to 1.4 g/L at natural pH with simulated wastewater. To study the effects of catalyst dosage, the experiments were conducted under the conditions of actual pH and pollutant concentration of 0.27 g/L(0.2 ml). The results showed that the monocrotophos removal increased with increase in ZnO dosage up to 1.2 g/L after which a decrease in removal was observed. The maximum removal achieved was 51% with 1.2 g/L of ZnO in UV/ZnO process. The initial increase in removal with increase in dosage was due to the increase in number of active sites, which in turn increased the hydroxyl radical generation due to increase in surface area and light absorption. Further increase in catalyst dosage above the optimum level resulted in decrease in light penetration and deactivation of activated molecules due to collision with the ground state molecules. The effect of catalyst concentration on ZnO photocatalysis is shown in Figure 3.2

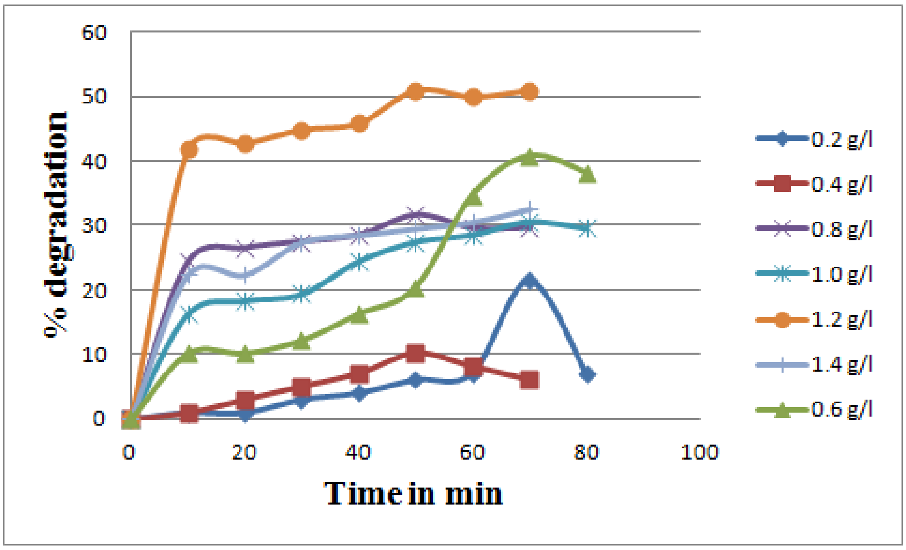

Figure 3.2. Effect of catalyst dosage ZnO photocatalysis

3.3. Effect of contact time

The experiments were conducted in the natural pH condition, monocrotophos concentration 0.27 g/L and catalyst dosage of 1.2 g/L. The results obtained for the effect of contact time on monocrotophos removal for UV/ZnO is represented in Figure 3.3. Degradation proceeds rapidly in the presence of nano catalyst showing sharp decrease in the concentration of monocrotophos for the first 60 minutes, further proceeding slowly. The slowing down of degradation after 90 minutes is probably due to lack of OH•. Therefore, increase in illumination time more than 60 min does not lead to greater photodegradation efficiency of Monocrotophos.

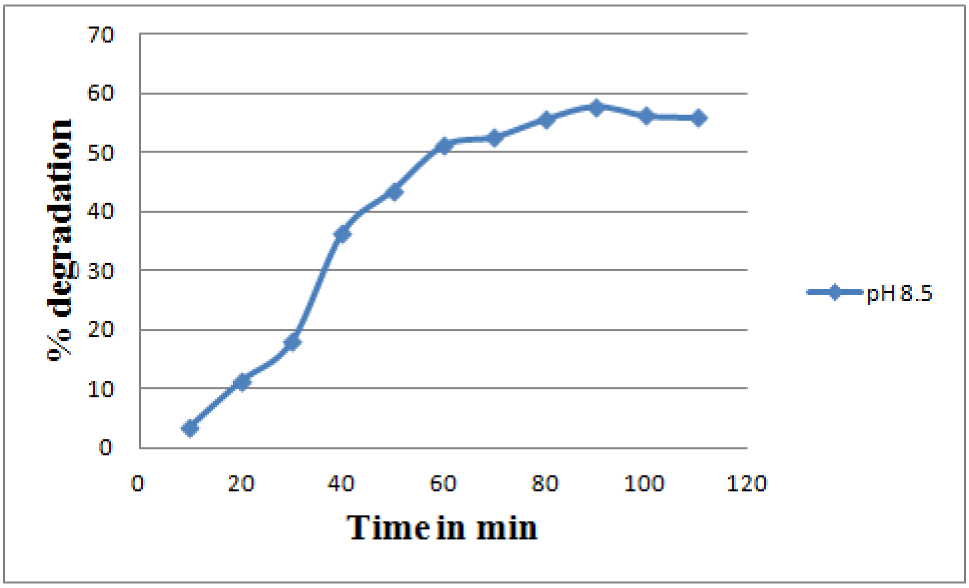

Figure 3.3. Effect of contact time

3.4. Effect of Initial pollution concentration

The experiments were conducted in the concentration range of 0.27 g/L to 0.67 g/L by maintaining other operating parameters such as pH 8.5, ZnO dosage of 1.2 g/L and contact time of 90 minutes. The monocrotophos removal decreased with increase in the initial concentration of pesticides. It was found that at lower concentration, hydroxyl radicals were sufficient to attack the pesticide molecules. But with increase in concentration, the catalyst surface available to generate hydroxyl radical was not sufficient enough to attack pesticide molecules thereby decreasing the degradation. Thus surface adsorption process of paramount importance in controlling the degradation of monocrotophos. The effect of initial pollution concentration is shown in Figure 3.4.

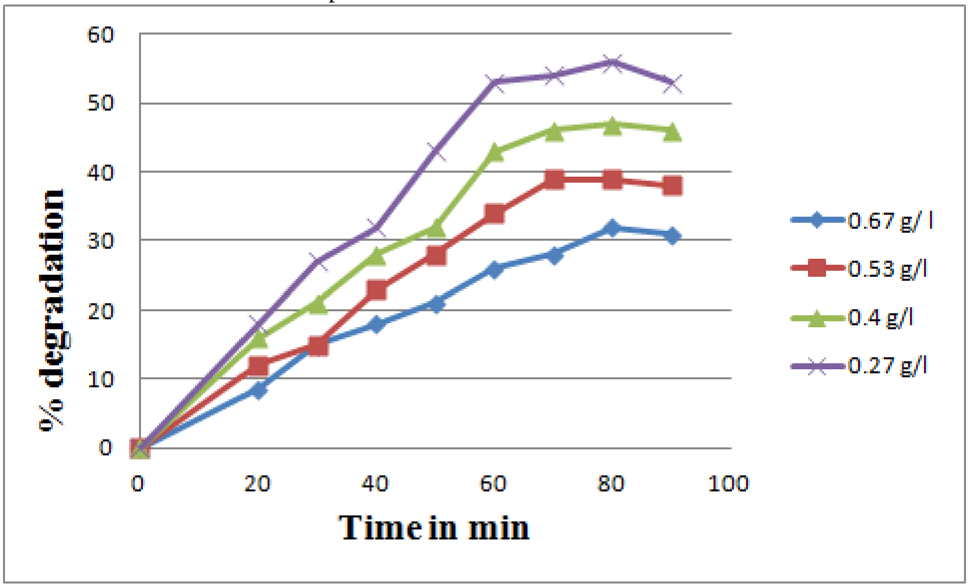

Figure 3.4. Effect of Initial pollution concentration

4. CONCLUSION

The UV/ZnO process is highly effective in degradation of monocrotophos. Slightly alkaline pH leads to maximum degradation of monocrotophos and increase in pollutant concentration decreases the degradation of pesticide. Screening effect of catalyst increased turbidity of the solution and ultraviolet rays gets scattered, hence the number of active sites on the ZnO surface becomes constant. The maximum degradation rate achieved by UV/ZnO processes is 74%. This treatment method achieves the standard prescribed by the regulating authorities in terms of COD content, but the amount of pesticide concentration was slightly higher than the prescribed standard which needs further study viz: increasing contact time, addition of hydrogen peroxide to induce hydroxyl radicals in shorter time and UV/ZnO/H_2O_2 processes.

REFERENCES

[1] APHA (1998), 'Standard methods for the examination of water and wastewater', (American Public Health Association/American water works association/Water Environment Federation, Washington, DC). 20th edn.

[2] Aandan.S, A.Vinu, K.L.P. Sheeja Lovely, N.Gokulakrishnan, P.Srinivasu, T.Mori, V.murugesan, V.Sivamurugan and K.Ariga (2007), 'Photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension', Journal of Molecular Catalysis A: Chemical 266, pp.149- 157.

[3] Augustine Amalraj and Anitha Pius (2015), 'Photocatalytic degradation of monocrotophos and chlorpyrifos in aqueous solution using TiO2 under UV radiation', *Journal of Water Process Engineering 7*, pp. 94–101.

[4] Augustine Chioma Affam and Malay Chaudhuri (2013), 'Degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous solution by TiO2 photocatalysis', *Journal of environmental management 130*, pp. 160

[5] Abhilash.P.C, Nandita Singh. (2009),'Pesticide use and application: An Indian Scenario', Journal of Hazardous Materials 165, pp. 1- 12.

[6] COINDS, Wastewater Management in Pesticide Industry, CPCB Report No. COINDS/47/1993-94.

[7] Gomathi Devi L., Narasimha Murthy B. and Girish Kumar S. (2009),'Photocatalytic activity of V^{5+}, MO^{6+} and Th^{4+} doped polycrystalline TiO2 for the degradation of chlorpyrifos under UV/Solar light', *Journal of Molecular Catalysis A: Chemical 308(2009)*, pp. 174-181.

[8] Hasnidawani.J.N, H.N.Azlina, H.Naarita, N.N.Bonnia, S.Ratim and E.S.Ali (2016), 'Synthesis of ZnO Nanostructures Using Sol_Gel Method', Procedia Chemistry 19, pp. 211-216.

[9] Jurablu.S, M.Farahmandjou, and T.P.Firoozabadi (2015),'Sol- Gel Synthesis of Zinc Oxide (ZnO) Nanoparticles: Study of Structural and Optical Properties', Journal of Sciences, Islamic Republic of Iran 26(3): 281-285.

[10] Kausar Harun, Norsakinah Mansor, Zainal Arifin Ahmad and Ahmad Azmin Mohamad (2016), 'Electronic properties of ZnO nanoparticles synthesized by Sol-gel method: A LDA+U calculation and experimental study', Procedia Chemistry 19, pp. 125-132.

[11] Manual for analysis of Pesticide Residue in foods - Food Safety and Standards Authority of India (fssai) (2016).

[12] Ministry of Chemicals and Fertilizers –Annual Report 2016 -2017

[13] Major use of Pesticides Registered under the Insecticide act 1968, year 2009.

[14] Sadraei R (2016) 'A simple Method for Preparation of Nano – sized ZnO', Research and Reviews: Journal of Chemistry.