

Photo-assisted Degradation of Imidan Insecticide in Aqueous Solution of TiO₂

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Abstract—Imidan insecticide controls a broad spectrum of pests on a variety of fruit, vegetable, nut and ornamental crops due to its active ingredient of phosmet. But it is quite toxic compound for all kind of biotic species and mostly spread through inhalation and eye contact. Focal point of this research paper is to degrade the Imidan insecticide in the presence of artificial UV light with the optimization of all those parameters which affect to the degradation rate of Imidan and cost benefits were also considered during the research because all the significant trials were conducted at room temperature and pressure. In this case, Imidan was most effectively 92.5% degraded and 70% mineralized at the optimized catalyst concentration of 0.75 mgL⁻¹, pH 4 and oxidant concentration of 0.725 gL⁻¹. The discussed results show the probable application of this technology as a good alternative to the conventional method for the treatment of toxic compound

Key words: Insecticide, TiO₂, Oxidant, Photocatalysis

1. INTRODUCTION

Huge amounts of synthetic insecticide are used worldwide for increasing the turnover of crop production. Consequently, these compounds reach as foreign contaminates in different natural resources like air, water, soil and disturb their ecological balance. So presence of large number of insecticide has been appeared in water during last decades. The insecticide infected water may lead to various health issues like headache, vomiting, irritation and many more. Even conventional treatment plants have low biodegradability related to these compounds. Because physicochemical and biological treatment has a lot of limitations and sometimes it need pretreatment in order to achieve a high biodegradability. Researchers have applied different advanced treatment methods like thermal degradation, microbial degradation etc. But since it has higher cost and sophisticated actions, these methods are not more reliable. To facilitate the system by removal of all the limitations, advanced oxidation method is one of the processes, which is mostly associated with the complete destruction of hazardous compounds.

AOPs (Advanced oxidation process) consist of “clean” methods and reagents, e.g. ultraviolet irradiation, ultrasound treatment, ozonation and hydrogen peroxide oxidation, which can proficiently be applied also in combination [1]. These processes are characterized by the formation of hydroxyl radicals, which demonstrate high reactivity and efficiency in oxidizing a huge variety of pollutant [2]. In this regard heterogeneous photo catalysis has attracted a great attention towards degradation of insecticide at low cost. It is mediated by semiconductor (TiO₂) which is one of significant catalyst and has been used in many different photo catalytic reactions [3]. The photocatalytic oxidation with TiO₂ as a catalyst uses only UV fraction of the solar radiation, which forms about 4-6 % of the total spectrum [4].

Imidan (N-Mercaptomethyl phthalimide) is one of the organophosphorous insecticide. Imidan may be used during dormancy to control specified insects in different crop application like tree fruits (almonds, Blueberries, apple, grapes and pears) and nuts. On the other hand, it also has acute effect due to its active ingredient “organophosphate” which produces cholinesterase inhibition in animals. Exposure of this pesticide may be more harmful if inhaled, absorbed into skin and if it come in contact with eyes. Symptoms of cholinesterase inhibition include in carination, salivation, sweating, headache, muscle, nausea, twitching, tremors, blurred vision, tears, diarrhea, abdominal cramps and chest discomfort [5]. This insecticide behaves as a toxic compound to aquatic life also.

The aim of present work is photocatalytic degradation of technical grade Imidan insecticide. All the processes were optimized by varying the concentration of the catalyst, pH, H₂O₂, COD test and spectrophotometric studies were used to respectively measure the extent of mineralization and degradation.

2. MATERIALS AND METHODS

2.1 Reagents and Samples

Imidan insecticide (Fig. 1) was supplied by Sigma Aldrich in technical grade form. Chemical used in the experiment was TiO_2 (Degussa P-25) which has BET surface area $50 \text{ m}^2\text{g}^{-1}$, H_2O_2 (30% v/v). COD reagents like Ferroin indicator, $\text{K}_2\text{Cr}_2\text{O}_7$, FAS (0.1N) were also used to determine the extent of mineralization. Distilled water was used for making the solution throughout the process at the conductivity of $0.5 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C . pH of sample was adjusted by using H_2SO_4 (0.1N) and NaOH (0.1N).

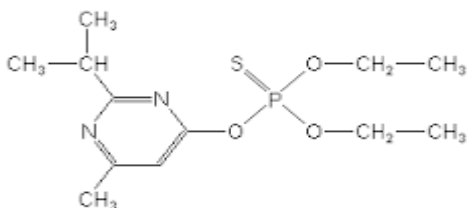


Fig. 1: Chemical structure of Imidan

2.2 Experimental setup and Procedure:

Immersion well reactor was used for the photocatalysis process and the whole process occurred in batch system. This photo reactor is fabricated of glass, ordered in cylindrical shape and also provided with cooling jacket system for maintaining the temperature. Medium pressure mercury lamp was used as sources of the UV light at the wavelength of 254 nm [6]. Aeration system was provided for source of oxygen as well as for mixing purpose.

Initial concentration of compound was 20 mgL^{-1} and a volume of 200 ml of aqueous solution was added every time in reactor with the different concentration of catalyst (TiO_2 in suspension form) and in some of case, oxidant (H_2O_2) was also added for increasing the number of OH radicals which lead to further increase degradation efficiency.

This solution was irradiated under UV lamp for required time with continuous mixing. Samples were taken from the reactor at regular interval of time with the using of syringe but before any analysis, the samples were filtered through $0.45 \mu\text{m}$ filter to remove the catalyst agglomerates. Results were repeated four to five times (depend on the experiment) for more accuracy.

2.3 Analysis

The degradation studies were carried out with help of UV-Visible double beam spectrophotometer at the wavelength of 239 nm. Decrease in graph of absorbance demonstrates the degradation of compound and reduction in value of COD shows the mineralization. The entire experimental results were optimized under all the parameters.

3. RESULTS AND DISCUSSION

3.1 Effect of catalyst loading

Firstly photocatalytic degradation studies were conducted from a catalysts range of 0.25gL^{-1} to 1.25gL^{-1} in order to achieve an optimum dose at its natural pH for the irradiation period of 2 h. Experimentally it was observed that degradation rate increase with the increase in catalyst dose but after reaching a certain level (the optimum value). It starts decreasing because of hindrance in light penetration [7]. Following Fig. 2 shows that almost highest 90% degradation was achieved at catalyst concentration of 0.75 gL^{-1} .

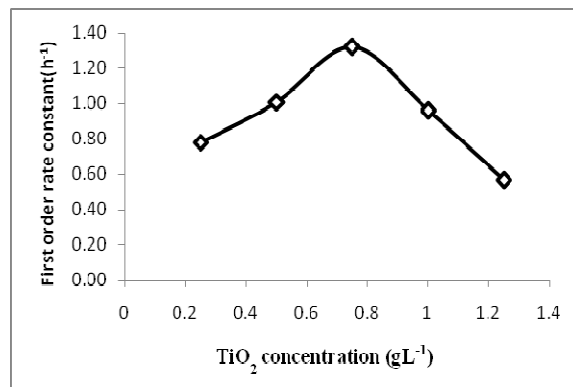


Fig. 2: Effect of TiO_2 concentration (Initial concentration= 20 mgL^{-1} , $\text{pH}=4$)

3.2 Effect of pH

pH is one of the most considerable factors for optimizing the result as an effect on the surface charge of catalyst which further influences to the adsorption of compound molecules on the catalyst surface[8]. Effect of pH on degradation rate was studied from a range of 3 to 7 at the optimized concentration of catalyst. Following Fig. 3 shows the influence of pH on the degradation of Imidan insecticide. 90% degradation was observed after the irradiation period of 2 h at their natural pH 4. No need of alteration in pH is required.

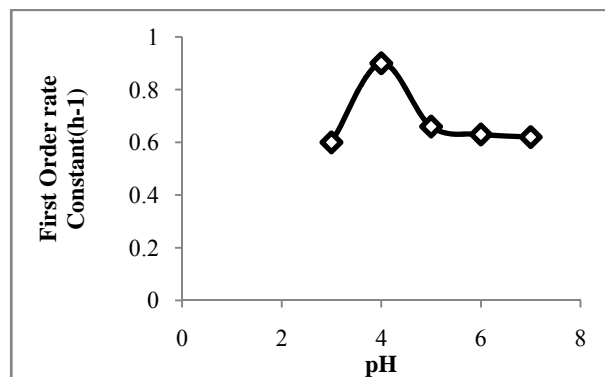


Fig. 3: Effect of pH (Initial concentration= 20 mgL^{-1} , $\text{TiO}_2=0.75 \text{ gL}^{-1}$)

3.3 Effect of oxidant (H₂O₂)

To determine the effect of oxidant on the degradation rate. Experimental study was conducted by the oxidant (H₂O₂) concentration range of 0.36 to 7.25 gL⁻¹ at the optimal value of pH and catalyst dose. As the degradation rate is affected by quantity of hydroxyl radicals. So addition of oxidant provides extra radicals which lead to additional support for degradation of compound. From Fig. 4, it can be marked that additional 2% degradation was achieved at the optimal oxidant dose of 0.725 gL⁻¹ within 2 h. But at the further addition of oxidant dose beyond its optimal value, rate of reaction decreased because of the scavenging of OH[•] radicals [9].

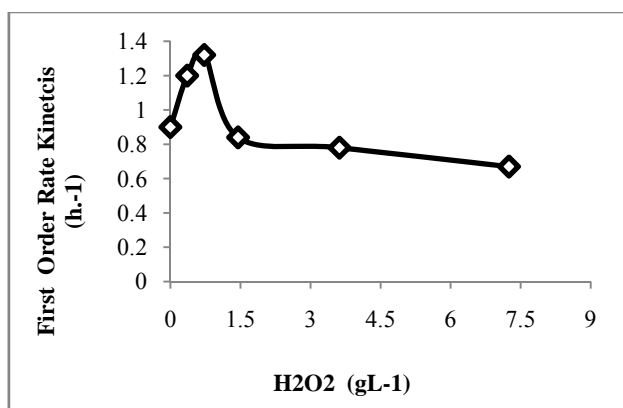


Fig. 4: Effect of H₂O₂ (Initial concentration=20 mgL⁻¹, TiO₂=0.75 gL⁻¹, pH=4)

4) Study of degradation and demineralization under photocatalytic condition

When Imidan insecticide went under photocatalytic degradation under all optimized conditions i.e. TiO₂ =0.75 gL⁻¹, pH=4, oxidant concentration= 0.725 gL⁻¹. Result shows (figure-5) that degradation and mineralization was respectively achieved 92.5 and 70% within 120 min. of study.

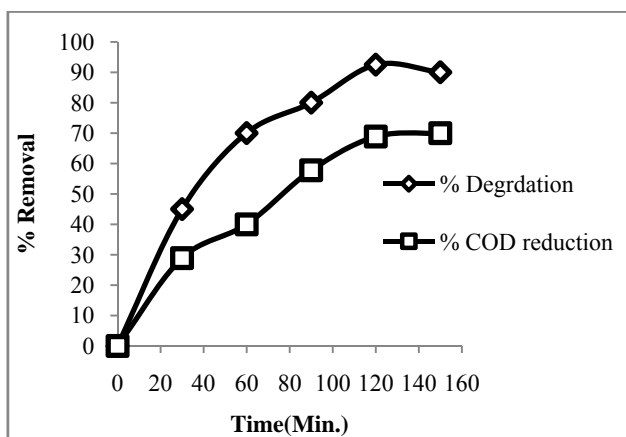


Fig. 5: Study of degradation & demineralization (Initial concentration=20 mgL⁻¹, TiO₂=0.75 gL⁻¹, pH=4, H₂O₂ Concentration=0.725 gL⁻¹)

4. CONCLUSION

Significant amount of Imidan in environment creates survival problems for terrestrials as well as for aquatic animal's at large scale. Due to its recalcitrant nature of this compound, it is prone to undergo the process of photo-assisted oxidative degradation in aqueous solution of TiO₂.

The report finding suggest also that UV light alone in absence of catalyst and oxidant is unable to provide sufficient degradation of recalcitrant compound .So various kind of parameters like catalyst dose ,pH , oxidant dose, initial compound concentration ,intensity of UV light extensively effect on degradation efficiency. So all the result were optimized under the catalyst dose of 0.75 gL⁻¹, pH of 4, oxidant concentration of 0.725 gL⁻¹ and 92% degradation was achieved only in 2 h of treatment where initial concentration of compound was taken 20 mgL⁻¹.

Future research must also investigate the efficacy of these technologies in the combination with other cost effective treatments such as sonolytic process in order to enhance the degradation efficiency.

REFERENCES

- [1] Selli E.,Claudia L., Bianchi., "Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO₂ and sonolysis", Journal of Hazardous Materials,153,3, 2008, pp 1136-1141
- [2] IbhadenA., "Heterogeneous Photocatalysis: Recent Advances and Applications",Catalyst,3,1,2013,pp 189-218
- [3] Xekoukoulotakisa, Nikolaos P., "Kinetics of UV-A/TiO₂ photocatalytic degradation and mineralization of the antibiotic sulfamethoxazole in aqueous matrices", Catalysis Today,161, 2011,pp163-168
- [4] Verma A.,Poonam, Dixit D., " Photocatalytic degradability of insecticide Chlorpyrifos over UV irradiated Titanium dioxide in aqueous phase" ,International Journal Of Environmental Sciences,3,2, 2012,pp 733-755
- [5] "Material safety data sheet of Imidan insecticide", generated by the gowan Canada foundation,,2014.
- [6] Agarwal V., " Degradation of monocrotophos pesticides using the advanced oxidation method", Journal of Environment and Waste Management,1,1, 2014,pp 002-010
- [7] Malato, S., Blanco J.,Maldonado M.L., Fernandez-Ibañez P., Campos A., "Optimising solar photocatalytic mineralisation of pesticides by adding inorganic oxidising species; application to the recycling of pesticide containers", Applied catalysis B: Environmental, 28,3-4,2000,pp 163-174.
- [8] Wang N., Zhu li., "Highly photocatalytic activity of metallic hydroxide/titanium dioxide nanoparticles prepared via a modified wet precipitation process". Journal of Photochemistry and Photobiology A: Chemistry,198,2-3,2008,pp 282-287.
- [9] Kavitha, S. K. and Palanisamy, P.N., "Photocatalytic and sonophotocatalytic degradation of reactive red 120 using dye sensitized TiO₂ under visible light",World academy of science ,Engineering and technology, 73,2011,pp 1-6