Malathion Pesticide Degradation by Advanced Oxidation Process (UV-Irradiation)

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Abstract— *This study investigated the degradation of commercially used organophosphorous pesticide malathion in aqueous solution by UV-Irradiation process. The process was optimized by varying different parameters such as operating pH, TiO_2 loading, H_2O_2 concentration and initial pollutant concentration. It was observed that COD removal were 91.6 % for 2 ppm initial concentration of malathion and under optimized condition TiO_2 loading 3gm/L, pH 6, and H_2O_2 concentration of 0.625 ml/50ml solution in 16 hours. This study indicates that degradation by UV-Irradiation process could be used as efficient and environmental friendly technique for the degradation of bio-recalcitrant organic pollutants.*

Keywords— *Pesticide, malathion, Aqueous solution, degradation, UV-irradiation, COD,UV Spectophotometer, TiO_2,*

I. INTRODUCTION

By the excessive use of pesticides in agriculture, large quantities of waste water generated in different countries which is extremely toxic [1]. Pesticides are those substances or mixture of substances which intended for preventing, destroying, repelling or mitigating any pest. For agricultural and non-agricultural activities, a large number of pesticides and insecticides are currently in use worldwide for several benefits, includes crop protection, preservation of food and materials and prevention of vector-borne diseases etc. [2]. Due to wide use of pesticides, they have become the second largest contaminant in drinking water and food. Depending on the usage of pesticides, the pesticides classified into insecticides, herbicides, nematicides, micro-biocides, fungicides [3].

Malathion is one of the highly hazardous organophosphate pesticide out of the major groups of pesticides that is widely used and easily available in countries. This pesticide controls pests on a variety of crops. Also malathion pesticide is acutely toxic to birds and humans, and widespread bird kills [4]. Malathion can be absorbed through various routs like ingestion, inhalation and skin contact. When inhaled, it affects the respiratory system. To achieve the removal of this compound is necessary but the actual state performance of conventional methods (primary, secondary and tertiary) are clearly not suitable to treat toxic, non-biodegradable organic pollutants and new improved treatments have to be developed and tested. To overcome the inconveniences of conventional treatment methods, Advanced Oxidation Techniques (AOP's) have emerged in the last decades, in particular for the treatment of pesticides. These techniques are basically very ecofriendly & less time consuming technology and most basic advantage of these technology is completely destruction of any toxic compounds into nontoxic ending products and it can be easily carried out at room temperature and atmospheric pressure. AOP's differ from the other treatments processes

because wastewater compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated, there is no need to dispose of materials [5]. Basic principle behind of this technology is production of OH° radical which has high oxidation potential and mainly its non-selective property. These OH° radicals can easily react with the toxic compound due to its high potential capability and change into nontoxic ending products.

UV-Irradiation process is an advanced oxidation process (AOP) which include homogeneous and heterogeneous photocatalytic processes. AOP with the highly reactive hydroxyl radical (OH°) as the main oxidative species and either hydrated electrons or hydrogen atoms as reducing species can degrade the pollutants present in water. The use of UV irradiation in absence of any catalyst to irradiate a polluted aqueous solution, this method does not fully decompose the organic pollutant molecule but instead generates intermediates from the pollutant molecules, which could be more hazardous than the parent pollutant molecule [6].

The general mechanism of the photocatalytic reaction process on irradiated TiO_2 is shown as follows [7]
Absorption of the photon energy in the form of UV light on TiO_2 particles and there is electron-hole pair formation.

$$TiO_2 + hv \rightarrow TiO_2\text{-} + OH° \text{ (or } TiO_2^+)$$
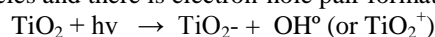
Generation of extremely reactive but short lived hydroxyl radical (OH.) by hole trapping.

$$H^+ + H_2O \rightarrow OH° + H^+$$
$$H^+ + OH^- \rightarrow OH°$$
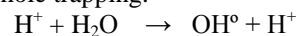
Surface reaction i.e. oxidation of the pollutant molecules under UV light.

$$OH° + O_2 + C_xO_yH_{(2x-2y+2)} \rightarrow xCO_2 + (x-y+1)H_2O$$
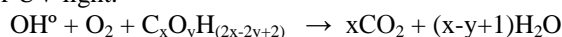
Radical recombination (energized holes and electrons can either recombine)

$$TiO_2^- + OH° + H^+ \rightarrow TiO_2 + H_2O \text{ (recombination)}$$

II. EXPERIMENTAL WORK

A. Chemicals

Malathion (CAS number 121-75-5) and Hydrogen peroxide (30%, w/w) and Rutile type TiO2 was obtained from Sigma-Aldrich and Sterling Labcare and used without further purification. Potassium hydrogen phthalate (KHP) is used for theoretical COD. All other chemicals used were of analytical grade.

B. Analytical Methods

Chemical Oxygen Demand (COD) was determined according to the 'APHA' Standard Method [9]. When sample

contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 so as to decompose hydrogen peroxide to oxygen and water [8-10].

C. Experiment Setup

The heterogeneous photocatalytic batch reactor was used to carry out the reaction. The SAIC made 125 W UV (Hg vapour) lamp was used to irradiate the sample. The Rutile type TiO_2 was used as photocatalyst. Initially the heterogeneous photocatalytic oxidation experiment with malathion was conducted in presence of aeration in the photocatalytic reactor for 16 hr. The concentrations were used as 2 mg/L of malathion. The dark adsorption test was carried out with continuous aeration in absence of UV light for 30 minutes. We observed there was 10 to 20 % reduction in absorbance and COD. Finally, the main reaction was carried out in presence of UV light and getting continuous decrease in their absorbance and COD of malathion. The schematic representation of the photoreactor is shown in figure 1.
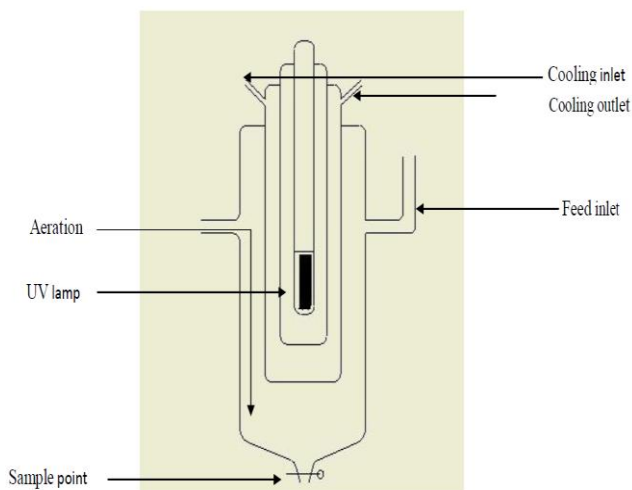

Fig. 1. Schematic representation of the photocatalytic reactor.

D. Experiment Procedure

Pesticides aqueous solution was prepared 100 ppm of malathion in distilled water. It was stored in a cold room at 4 ° C. Batch UV-Irradiation was performed for 50 ml aqueous solution of the malathion pesticide at different concentration and the pH was adjusted by using 0.1 M NaOH or 0.1 M H_2SO_4. After that TiO_2 and H_2O_2 were added and the sample was kept in experimental setup for reaction. At the selected reaction time, a sample was taken and filtered through filter paper for COD measurement. After treatment of 4 hours GC-MS analysis was done from CENTRE OF EXCELLENCE VAPI, GUJARAT, INDIA and found there were formations of intermediates in malathion degradation experiment.

III. RESULT AND CONCLUTION

A. Effect of pH

The pH plays an important role in the photocatalytic process of various pollutants [11]. To determine the optimum pH in this study the experiments were conducted in the range 2-9. And other operating condition was TiO_2 loading 3 gm/L and malathion concentration 2 ppm, H_2O_2 Concentration 0.625 ml/50 ml solution. The effect of pH for malathion degradation in terms of COD is shown in figure (2). it is observed that in the illumination TiO_2 system, the effect of pH of the solution on the degradation rate can be explained mainly by the surface charge of TiO_2 [12]. The point of zero charge (pzc) of the TiO_2 is widely reported at pH=6.5. The TiO_2 surface is negatively charged in basic solution and positively charged in acidic solution [13]. Electrostatic attraction or repulsion between the ionic form of the organic compound (anionic or cationic) and the catalyst's surface and thus consequently enhances or inhibits the efficiency of photo-degradation respectively [13]. In this study the degradation of pollutant significantly increases in acidic suspension compound to that in alkaline suspension.
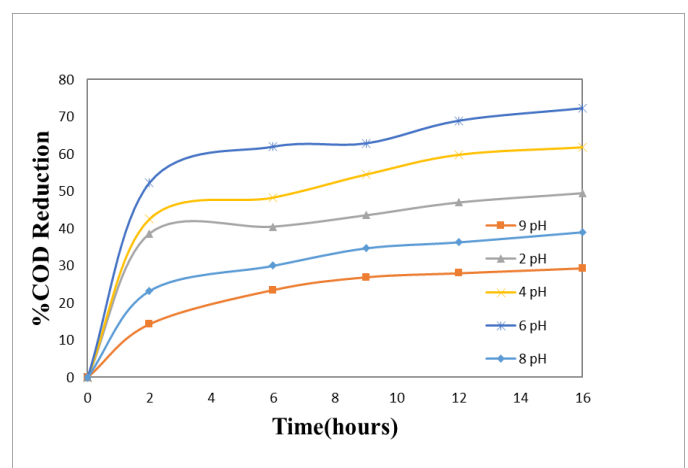

Fig. 2. Effect of pH for malathion degradation in terms of COD.

B. Effect of TiO_2 Loading

It has been reported that the increase in the number of TiO_2 particles increases the number of contaminated molecules absorbed and the number of photons absorbed [14]. Therefor the degradation efficiency can be enhanced with increasing TiO_2 concentration due to the increase in total surface area available for contamination adsorption. To determine the optimum TiO_2 loading experiments were performed in the degradation at different catalyst concentration ranging from 1gm/l to 6 gm/l. And other operating conditions were malathion concentration 2 ppm, pH 6, H_2O_2 concentration 0.625 ml/50 ml solution. The effect of TiO_2 loading for malathion degradation in terms of COD is shown in figure (3). The efficiency decreases slightly when the amount of TiO_2 is above 3 gm/l, the reason for this decrease in degradation rate are: (1) decrease in light scattering and opticity of TiO_2 particles at high concentration. (2) decrease in the number of surface active sites due to aggregation of TiO_2 particles at high concentration [15].
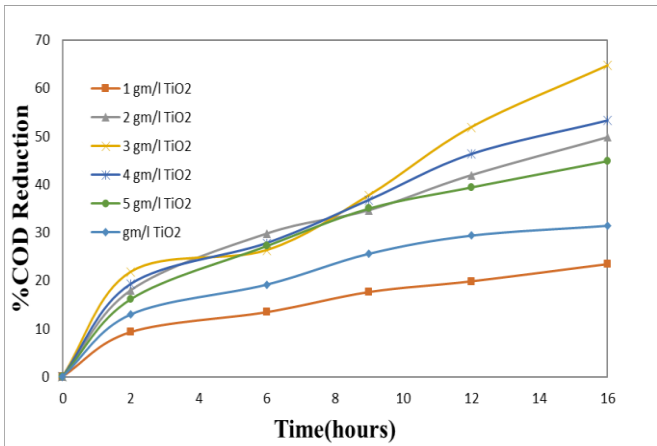
Fig. 3. Effect of TiO$_2$ loading for malathion degradation in terms of COD.

C. Effect of H$_2$O$_2$ Concentration

In order to enhance the photo-degradation rate of malathion under UV light, an oxidant (H$_2$O$_2$) is added into a semiconductor suspension. The experiments were performed by varying the hydrogen peroxide (H$_2$O$_2$) concentration from 5 ml/L to 20 ml/L. And other operating condition were malathion concentration 2 ppm, pH = 6, TiO$_2$ loading = 3 gm/L. And reaction was maintained up to 16 hours. The effect of H$_2$O$_2$ concentration for malathion degradation in terms of COD is shown in fig. 4.
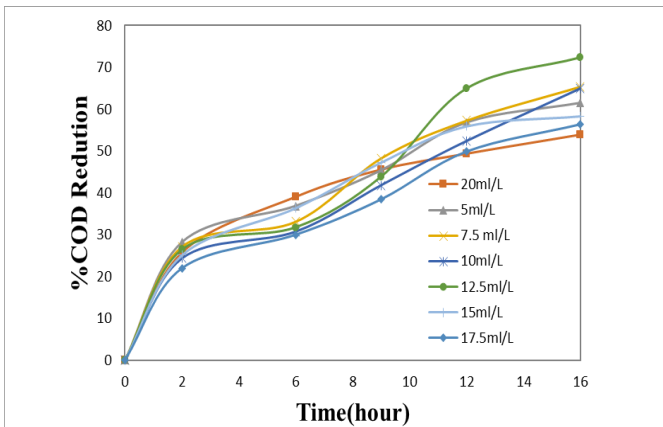

Fig. 4. Effect of H$_2$O$_2$ Concentration for malathion degradation in terms of COD.

It is observed that the overdose of H$_2$O$_2$ retards the malathion photocatalytic degradation rates. The slight rate improvement at lower H$_2$O$_2$ dosages is probably due to the enhancement of the photocatalytic activity by providing an additional oxidant source and by reducing the rate of recombination between holes and electrons in the activated dioxide particles [16]. H$_2$O$_2$ shows two main functions in the process of photocatalytic degradation. The acceptance of photo generated electron by H$_2$O$_2$ from a conduction band and thus promotion of the charge separation. Also formation of OH$^\circ$ radical by H$_2$O$_2$ as shown in equation (1). At high H$_2$O$_2$ concentration, it acts as a scavenger, as shown in the following equations [17]:

$$H_2O_2 + OH^\circ \rightarrow HO_2^\circ + H_2O \tag{1}$$

$$HO_2^\circ + OH \rightarrow H_2O_2 + O_2 \tag{2}$$

D. Effect of Initial Concentration

The effect of initial concentration of malathion was studied at different concentrations. The malathion degradation was studied at 2, 4, 6 ppm, of initial concentration respectively. The effect of initial concentration in terms of COD reduction is shown in figure (5). It is observed that there was not enough dosage of TiO$_2$ to provide active radicals for the degradation of malathion at higher concentration. Also higher concentration leads to more formation of byproducts, which might have absorbed some photons or consumed additional active radicals [18]. The mineralization of malathion monitored under the UV absorbance spectra. After 16 hrs disappearance of malathion was observed different for different concentration.
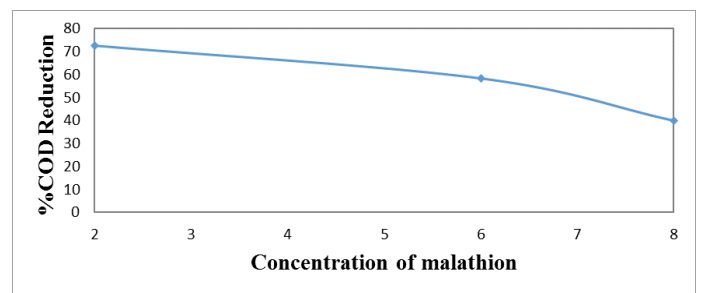

Fig. 5. Effect of initial concentration in terms of COD reduction.

E. kinetics of pesticide Degradation

The kinetics of degradation of the malathion pesticide in aqueous solution was studied. A general reaction rate expression for kinetics of malathion degradation has been used [19]. The mineralization rate of the pesticide followed the first order kinetics according to the eq. (1) [20]

$$\ln (C/C_0) = - k*t \quad ......(1)$$

where C and C$_0$ are the total malathion pesticide concentration at time t and zero and k is the rate constant. The rate constant k was obtained by plotting ln(C/C$_0$) vs t and the slope of the straight line was used to determine the function.

F. Degradation at Optimum Conditions

At a reaction time of 16 hours it was observed that the overall degradation of malathion in terms of COD is 91.6%. Initially the process was optimized by varying parameters such as operating pH, TiO$_2$ loading, H$_2$O$_2$ concentration and initial pollutant concentration. To find the optimum pH the experiment was conducted in range of 2-9 pH and for TiO$_2$ loadings experiment were performed at the catalyst concentration ranging from 1-6 gm/l TiO$_2$, for H$_2$O$_2$ concentration the experiment was conducted by varying the H$_2$O$_2$ concentration from 5-20ml/l, for initial malathion concentration the malathion degradation was studied at 2,4,6 ppm. The optimum conditions were observed as 2 ppm initial concentration of malathion and TiO2 loading 3gm/L, pH 6, and H$_2$O$_2$ concentration of 0.625 ml/50ml solution.

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