Degradation of Malathion in Aqueous Solution by Photocatalytic Reaction Using TiO_2

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Abstract: *Photocatalysis is a powerful method for the degradation of pollutants resulting from the wide use of pesticides. The aim of present investigation is to study the degradation of the pesticide, malathion in aqueous phase by photocatalysis in the presence of TiO_2 catalyst and UV light, to harmless products. Reaction is carried out in laminar flow reactor LFH-4 fitted with UV lamp. The extend of degradation is studied by varying the parameters like pH, catalyst composition, catalyst concentration and temperature. The degradation is found to be maximum at a catalyst loading of 4g/L, pH of 6and catalyst composition of 75% anatase and 25% rutile by weight.*

Keywords: *Photocatalysis, TiO_2 catalyst, malathion, pesticide degradation.*

1. Introduction

The widespread use of pesticides in agriculture has lead to serious environmental problems including ground water and surface water pollution. In India, pesticides are mainly used for the cultivation of cotton, rice, vegetables and fruits. Farmers are using about 45% of the pesticides for cotton cultivation, eventhough it accounts for about 55 cultivable area[1,2,3]. Synthetic pesticides have been popular because of their wide spread availability, simplicity in application, efficacy and economic returns. But they have huge environmental costs [1]. The pesticide contaminated water may lead to the serious health problems such as vomiting, nausea, diarrhea, hypertension etc., if taken above the permissible limits.

Malathion is an organophosphorus pesticide used in public health, residential and agricultural settings. Malathion has a broad range of use with target pests in the orders dipterans, Lepidoptera, hemiptera, coleopteran, and other orders. Malaxon is an oxygen analogue of malathion and it can be found either as an impurity in malathion product, or can be generated during the oxidation of malathion in air or soil[4]. Malathion itself is of low toxicity; however, the absorption or ingestion into the human body readily results in its metabolism to malaoxon, which is substantially more toxic. Acute exposure to extremely high levels of malathion will cause body-wide symptoms whose intensity will be dependent on the severity of exposure. Possible symptoms include skin and eye irritation, cramps, nausea, diarrhea, excessive sweating, seizures and even death. Malathion present in untreated water is converted to malaoxon during the chlorination phase of the water treatment. So malathion should not be used in a source for drinking water, or any upstream waters[1].

Advanced oxidation processes (AOPs) have received increasing attention as an alternative for treating polluted waters. Among these processes, heterogeneous photocatalysis is one of the most promising. It has already been used successfully for the destruction of a great variety of organic compounds.

S K Kansal etal. [5] studied the performance of a photocatalytic process for degrading catechol with titanium dioxide and zinc oxide catalysts. The study was carried out using photoreactor equipped with 4 UV tubes each of 30W. Response surface methodology was used for the analysis. The study found that the degradation occurs at a fast rate in the case of TiO_2 as compared to ZnO in the presence of both UV and solar radiation. On a comparative analysis of UV radiation with solar radiation for a 1000 mg/L sample complete degradation of catechol is achieved within 45 min under UV irradiation whereas it requires 150 min for the complete removal of catechol under solar irradiation. This study reported the optimal conditions for degradation of catechol as 2g/L of TiO_2 at a pH 6. The amount of oxidant sodium hypochlorite was found to be 0.95ml[5].

E. Evgenidou et al. [6] studied the degradation kinetics of dimethoate in water under different conditions such as substrate and photocatalyst concentration, temperature, pH and addition of oxidants. Experiments were carried out in a 500mL Pyrex UV reactor equipped with a diving Philips HPK 125W high-pressure mercury lamp. TiO_2 and ZnO were used as the catalysts. Shimadzu V-csh TOC analyser and a WTW spectrophotometer were used for the analysis of the solution concentration. TiO_2 was found to be the best catalyst with optimum conditions of 100mg/l catalyst , pH 6.5 ,oxidant concentration 10mg/l. This study reported an increase in degradation rate with temperature from 25^0C to 65^0[6].

Fadaei et al. [7] studied the photodegradation of two organophosphorus pesticides, malathion and diazinon, by sulfate radicals and bicarbonate radicals in aqueous solution. Also effect of the operational parameters such as pH, salt concentration, water type, H_2O_2 concentration and initial concentration of pesticides was studied. Analysis of pesticides was done using gas chromatography mass spectroscopy (GC-MS). This study observed maximum degradation of Malathion at pH 9 whereas most of the other studies observed maximum degradation in slightly acidic solution. Addition of hydrogen peroxide was observed to increase the UV degradation rate of malathion from 10mg/l to 30mg/l. This study analyses the variation in degradation rate with the nature of water and found that the presence of organic carbon in the water inhibits the degradation rate. Also this study found that sodium bicarbonate is more powerful inhibitor compared to sodium sulphate[7].

M H Dehghani et al. [8] used a different method for the degradation of malathion. Ultrasonic in this study was model ELMA. Six different initial concentrations of malathion (100, 300, 500, 200, 400, and 600 mg/L respectively) at different pH (3, 7, 9) and time (30, 45, 60, 90, 105 min) were investigated. Analysis of the samples was performed by using gas chromatography with flame ionization detector (GC – FID). This study observed that the optimum pH for sonolysis was 9. Their observation was that the degradation rate decreases with an increase in the initial concentration of malathion in the sample[8].

Anoop Verma et al. [1] studied the degradation of malathion of low concentration possibly present in the river water. This study was conducted by using malathion of 2ppm concentration. In this research the reactor was designed with an average UV intensity of 27-30 W/m^2. Samples were analysed using standard COD measurements. This study was concentrated on various parameters that affect the degradation rate. As per the observation in this study the degradation was low in the absence of catalyst and the use of TiO_2 has shown a maximum degradation at 3g/l of catalyst loading. Optimum pH of 6 and oxidant concentration (H_2O_2) of 2.5 ml/l were the outcomes of their study. A comparative study with the solar source of same intensity resulted in a higher degradation as compared to UV light[1].

In the present work, an attempt has been made to obtain an optimal setting of process parameters which may yield optimum degradation of the malathion present in the water. The parameters considered are catalyst composition, catalyst concentration, pH and temperature. The technology is suggested as a pre-treatment process in the water purification.

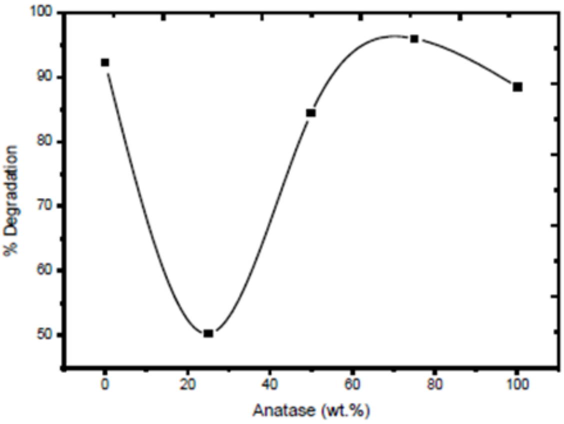

Figure: 1

2. Experimental

2.1. Procedure

The photocatalytic degradation of malathion in aqueous phase was done following the procedure of Verma et al [1]. A stock solution of Malathion (4 ppm) was prepared and 200mL of it was taken in the conical flask. To this, the required amount of catalyst (TiO_2) was added. For a minimum period of one hour, the solution was maintained in the dark to ensure complete adsorption equilibrium. The solution was then irradiated under UV lamp having an intensity of 30 Wm^{-2} with continuous stirring using a magnetic stirrer in laminar flow reactor LFH-4 for the required period. The sample was then filtered to remove the catalyst and analysed using refractometer. Experiments were conducted to study the variation in the extent of degradation with changes in parameters such as composition of catalyst, catalyst concentration, pH, temperature and effect of oxidant.

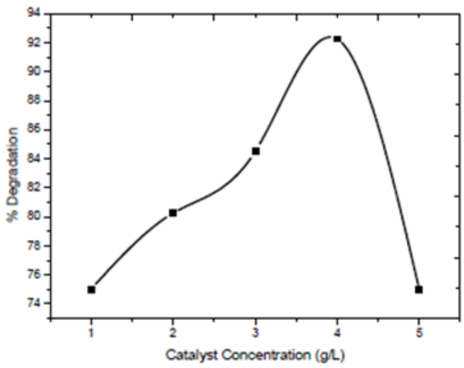

Figure:2

3. Results and Discussion

3.1 Effect of catalyst composition

To understand the effect of the form of TiO_2 catalyst on the degradation of malathion, experiments were conducted with a mixture of anatase and rutile grade TiO_2 in various proportions (0 to 100 wt.%) keeping temperature (30°C), pH (5), catalyst concentration (3g/L), stirrer speed (900 rpm) and time (6h) constant. The maximum degradation has occurred when the weight ratio of anatase to rutile is 75:30 and the results are shown in figure 1.

3.2 Effect of catalyst concentration

The number of photons and contaminated molecules absorbed are reported to increase with an increase in the number of TiO_2 particles [1,9,10]. So by increasing the TiO_2 concentration, the total surface area available for contaminant adsorption increases, and thus the degradation efficiency can be enhanced. By keeping pH (5), temperature (30^0C), composition of catalyst (50 wt.% anatase & 50 w.t% rutile), stirrer speed (900 rpm) and time (6hr) constant, catalyst concentration was varied from 1g/L to 5g/L. The results are given in figure 2. When the catalyst concentration increases from 1g/L to 4

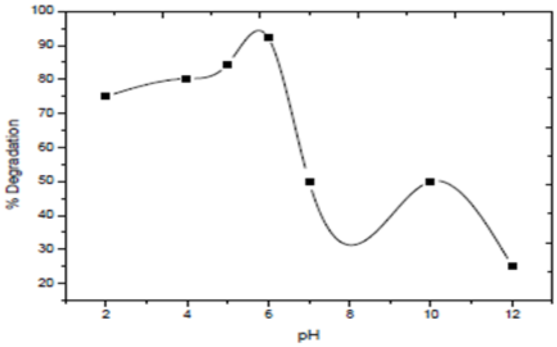

Figure:3

g/L, the degradation of malathion increases from 75% to 92.25%. The efficiency decreases slightly when the amount of TiO_2 is above 4 g/L. The reason for this decrease in degradation rate is the aggregation of TiO_2 particles at high concentrations causing a decrease in the number of surface active sites. Also the suspended particles of the catalyst will block the UV-light passage and increase the light scattering [1].

3.3 Effect of operating pH

The effect of pH is significant in the photocatalytic degradation of pollutants [1, 11]. By keeping temperature (30°C), composition of catalyst (50 wt% anatase & 50 wt% rutile), catalyst concentration (3g/l), stirrer speed (900rpm) and time (6hr) constant pH was varied. The observations are shown in figure 3. It is found that percentage degradation increases when the pH value increases from 2-6 and decreases thereafter in basic medium. The point of zero charge of TiO_2 is 6.3. So the TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution [1,12,13]. Electrostatic attraction or repulsion between the catalyst's surface and the organic molecule is taking place, depending on the ionic form of the organic compound (anionic or cationic) and thus consequently enhances or inhibits the photo degradation efficiency respectively [1]. In this study, the degradation of malathion is maximum at pH=6 which is close to the point of zero charge of the catalyst. When the catalyst has no charge, the molecules probably, are allowed to reach easily the catalyst's surface and achieve higher reaction rate.

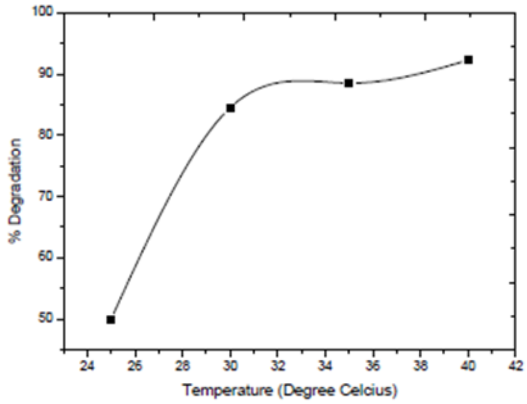

Figure:4

3.4 Effect of operating temperature

The effect of temperature in the degradation reaction was studied by keeping pH (5), composition of catalyst(50 wt% anatase & 50 wt% rutile), catalyst concentration (3g/L), stirrer speed (900rpm) and time (6hr) constant, varying the temperature of the stock solution from 30^0C to 40^0C. The influence of temperature on malathion degradation is shown in figure 4. As the reaction temperature increases, the degradation also increases.

4. Conclusions

The photocatalytic degradation of malathion in aqueous phase was carried out using TiO_2 catalyst. Under UV assisted irradiation, malathion gets degraded easily with TiO_2 catalyst having a composition of 75 wt.% anatase and 25 wt.% rutile. The optimum concentration of TiO2 photocatalyst is found to be 4 g/L. Other parameters suitable for maximum degradation of malathion include a pH of 6, temperature of 40^0C, oxidant H_2O_2 with a dose of 3 mL per 200 mL of the sample and a reaction time of 6 hours. Shallow pond reactors [1] can be scaled up using these results for effectively removing pesticides from water or wastewater.

Acknowledgements

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