



Studies on Photocatalytic Degradation of Monocrotophos in an Annular Slurry Reactor Using Factorial Design of Experiments

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ABSTRACT

Pesticide contamination of natural waters is posing serious threats to water supplies in many parts of the world. Heterogenous photocatalytic Oxidation with TiO_2 photocatalyst is emerging as an attractive technique for pesticide removal. Studies on Monocrotophos (MCP) a widely used pesticide in India, in an annular slurry photoreactor, revealed that the degradation rate is significantly affected by the initial pesticide concentration, pH of the solution and the catalyst concentration. Using a 2^3 central composite factorial design of experiments a quadratic polynomial model was fitted to predict the removal efficiency. The statistical analysis revealed that the coefficients for the main effects are significant. The MCP removals were in the range of 11 to 78 percent depending on the levels of the parameters studied.

Key words: Photo catalysis, Monocrotophos, TiO_2 , Slurry reactor, Factorial design, ANOVA and optimization

1.0 INTRODUCTION

A wide variety of pesticides have been used over the last 100 years in an effort to control pests and increase crop yield. A multitude of factors, viz physical, chemical and biological complicate the prediction of their fate and effects in natural environment (Alexander, 1972). Pesticides are also typically hydrophilic compounds, with low water solubility. But due to their higher solubility in fatty tissues, they get magnified within food chains. The possible chronic effects of these compounds are carcinogenicity, neuro toxicity and effects

on reproduction and cell development (Burrows, 2002). Because of its carcinogenic nature, there is a need for eliminating pesticides in surface water bodies. Limitations of conventional decontamination techniques have resulted in an intensive search for more efficient treatment techniques. Advanced Oxidation Process (AOP), which is based on the principle of highly reactive hydroxyl radical generation, has emerged as a sound alternate technique for treatment of hazardous pollutants (Hoffman et al.1995, Devipriya and Yesodharan 2005, Wang et al. 1999). Monocrotophos, a foliar insecticide is widely used for several crops in India and is potentially toxic to the aquatic environment. The decomposition of MCP in aqueous solution has been TiO_2 mediated photocatalysis has been re-

ported by Young Ku and In-Liang Jung (1998). Photocatalytic degradation of organophosphorus pesticides using thin films of TiO_2 has been studied by Zhao et al. (1995). The photocatalytic degradation of monocrotophos in aqueous solution was carried out by using ZnO, supports and supported ZnO by Anandan et al. (2006). Most of the literature reports on pesticide degradation are for relatively low concentrations while the pesticide concentration in contaminated ground water may be higher. Hence this study was aimed at evaluating the effectiveness of photocatalytic degradation of MCP in at higher concentrations and the results are presented in this paper.

2.0 MATERIALS AND METHODS

2.1 Materials

Technical grade pesticide Monocrotophos (80% purity) (Sriram Pesticides, India) and TiO_2 (pure anatase, surface area $15\text{m}^2/\text{g}$, CDH, India) were used in the experiments.

2.2 Experimental Studies

2.2.1 Adsorption Studies

Batch adsorption studies were performed with 100 mL solution of monocrotophos with initial concentrations in the range $5\text{-}25\text{ mg}\cdot\text{L}^{-1}$ in flasks containing 0.5 g of TiO_2 . The flasks were agitated at room temperature (28°C) at 100 rpm in a thermostatic rotary orbital shaker. The initial pH of the solutions was 7. Samples were taken at regular intervals and analysed for residual monocrotophos.

2.2.2 Degradation Studies

A schematic of the experimental setup is shown in Figure 1. The MCP degradation studies were carried out in an annular photo reactor consisting of an inner quartz tube of 2.5

cm dia and outer cylinder of 3.82 cm dia. A UV lamp (Philips, 9W) emitting predominantly at 254 nm wavelength provided the photonic energy required for degradation. A slurry of the solution MCP mixed with TiO_2 photocatalyst, from a well mixed feed tank, was continuously circulated using a peristaltic pump (Ravel Hitech, India) through the annular chamber. Samples were collected from the reactor at specific time intervals and analyzed by HPLC after filtration (Gelman GHP acrodisc $0.25\ \mu\text{m}$) to remove titania particles. The degradation studies were carried out over a range of pH from (5-9), initial concentration of pollutant ($10\text{-}20\text{ mg}\cdot\text{L}^{-1}$) and different catalyst concentrations ($2\text{-}6\text{ g}\cdot\text{L}^{-1}$).

2.3 Analytical Method

Concentration of residual MCP in the samples was analyzed by gradient HPLC method (Jasco Pu-2089 plus, Japan) with PDA detector using Agilent Eclipse PAH $5\ \mu\text{m}$ Column of dimension $10 \times 150\text{ mm}$. Acetonitrile and water (low conductivity) in the ratio of 70:30 was used as mobile phase at a flow rate of $1\text{ ml}\cdot\text{min}^{-1}$. The pesticide concentration was determined by measuring absorbance of samples and reading the corresponding concentration from a standard calibration.

2.4 Statistical Design of Experiment

Photocatalytic degradation is a complex process where there are possible interactions between the process variables. "A full factorial design which includes all combination for each factor is a powerful tool for analysing complex processes. (Ghosh and Swaminathan, 2004). The design consists of 2^k experiments where k is the number of variables in which each variable is placed either high (+) or low (-) level, two axial for each of variable and a fixed number of center point experiments in place of replicates. (Khuri et al, 1987). Thus a

total of 18 experiments (8 for the design, 6 for the axial points and 4 for center point) were

used as given in Table 2. The ranges of experimental variables are shown in Table 1.

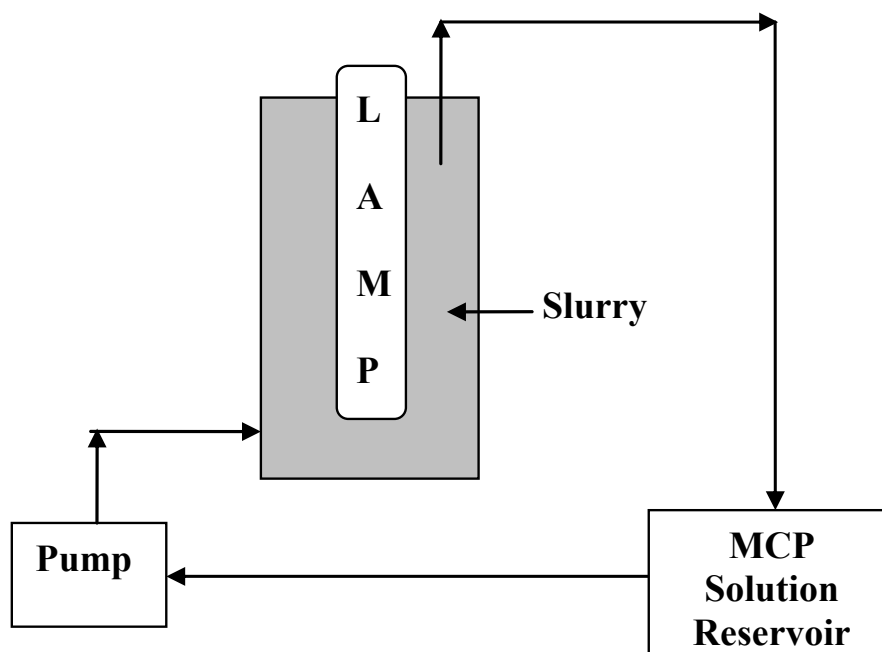


Figure 1 Schematic of annular slurry reactor

Table 1 Experimental range and levels of independent variables for MCP degradation

| Parameter | - α | -1 | 0 | +1 | α |
|---|------------|----|----|----|----------|
| Initial pesticide conc (mgL ⁻¹) | 6.59 | 10 | 15 | 20 | 23.41 |
| Catalyst conc (gL ⁻¹) | 0.64 | 2 | 4 | 6 | 7.36 |
| pH | 3.63 | 5 | 7 | 9 | 10.36 |

The data obtained through the statistically designed experiment was fitted to a second order polynomial equation.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$$

where Y is the response variable. The coefficients of the equation were estimated using a statistical program MINITAB 14 (Minitab Inc, USA). The regression analysis of the data was also done using the same program. The multiple correlation coefficient R and determination coefficient R² were used to test the validity

of the model. Analysis of Variance (ANOVA) was used to test the significance and adequacy of the model.

3.0 RESULTS AND DISCUSSION

Preliminary studies on the photo catalytic degradation of MCP were done by varying the parameter at a time. A typical degradation profile for 10 mgL⁻¹ is shown in Figure 2 at different time intervals.

Table 2 General factorial design for 3 variables for pesticide degradation studies

| Std | Run | Factor 1 | Factor 2 | Factor 3 | Removal Efficiency (%) |
|-----|-----|----------|---|---------------------------|------------------------|
| | | pH | Initial conc of pesticide mgL ⁻¹ | Catalyst gL ⁻¹ | |
| 1 | 1 | 5 | 10 | 2 | 78 |
| 2 | 14 | 7 | 15 | 7.36 | 55.1 |
| 3 | 13 | 7 | 15 | 0.64 | 42.57 |
| 4 | 3 | 5 | 20 | 2 | 40.1 |
| 5 | 18 | 7 | 15 | 4 | 48.9 |
| 6 | 4 | 9 | 20 | 2 | 35.1 |
| 7 | 6 | 9 | 10 | 6 | 51 |
| 8 | 8 | 9 | 20 | 6 | 30.2 |
| 9 | 9 | 3.64 | 15 | 4 | 62.03 |
| 10 | 5 | 5 | 10 | 6 | 62.87 |
| 11 | 11 | 7 | 6.59 | 4 | 60.28 |
| 12 | 16 | 7 | 15 | 4 | 47.8 |
| 13 | 17 | 7 | 15 | 4 | 56.57 |
| 14 | 15 | 7 | 15 | 4 | 58.72 |
| 15 | 7 | 5 | 20 | 6 | 37.6 |
| 16 | 12 | 7 | 23.41 | 4 | 53.84 |
| 17 | 10 | 10.4 | 15 | 4 | 11.86 |
| 18 | 2 | 9 | 10 | 2 | 57 |

3.1 Effect of Initial Concentration

Initial concentrations of reactants play a significant role in determining the rates of most of chemical and photochemical reactions. This was evident in the degradation patterns for the pesticides given in Figure 3. The degradation rate for MCP in the initial stages was faster, as seen from the steep slopes, followed by relatively slower removal efficiency at later stages. There was a significant reduction in the rate and extent of degradation of MCP as the initial concentration was increased from 10 to 25 mgL⁻¹. This may be attributed to several factors. At higher pesticide concentrations, there would be more adsorption of pesticide on TiO₂ resulting in a lesser

availability of catalyst surface for hydroxyl radical generations. The adsorption studies shown in Figure 4 clearly indicate that adsorption increases with MCP concentration. Similar result was observed by (Kormann et al, 1991) and they suggested the formation of several layers of adsorbed pesticide on photo catalyst surface, at higher pesticide concentrations. A higher pesticide may also almost adsorb more photons from the UV light thus reducing the photonic energy available for hydroxyl radical generation. Higher initial concentration also produces more intermediates which may competitively inhibit the pesticide degradation.

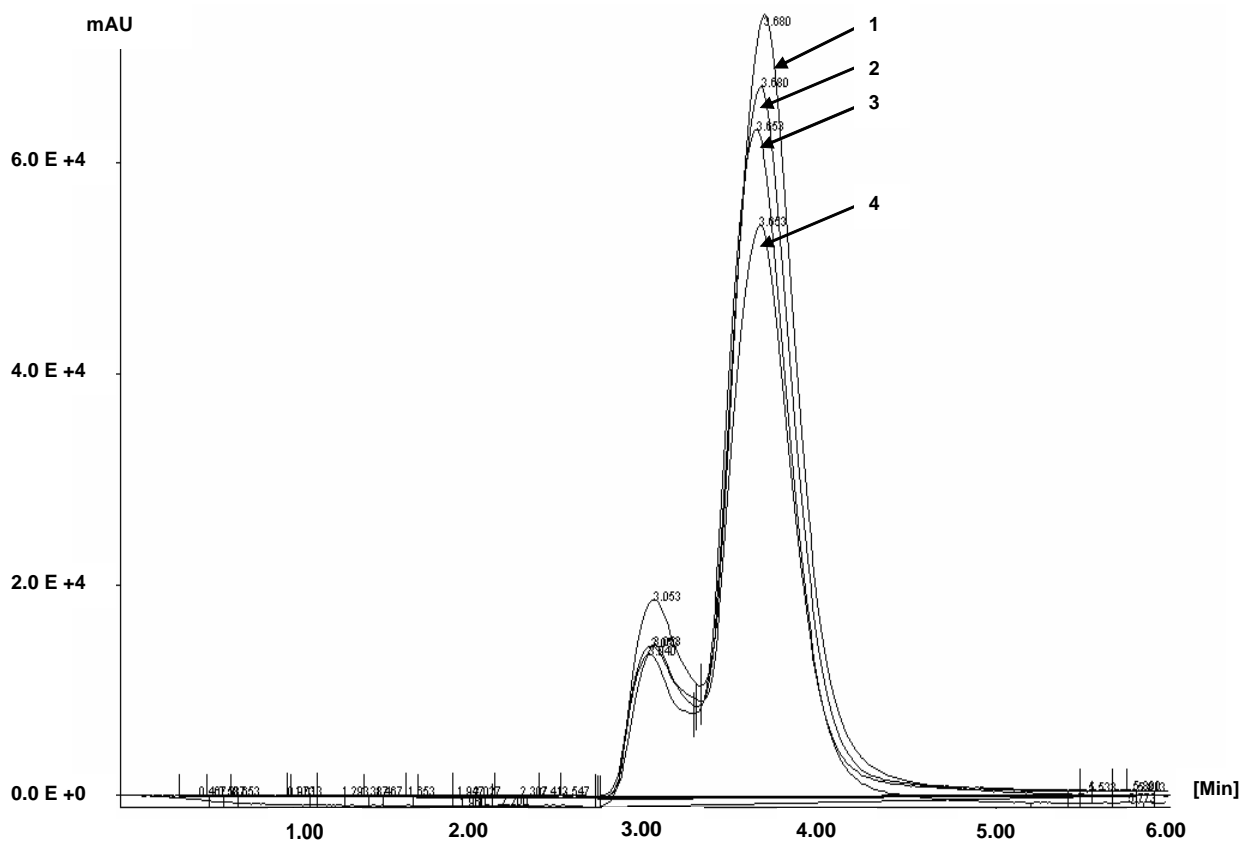


Figure 2 Typical degradation profile for MCP at 10 mgL⁻¹ initial concentration. Trace 1 - Chromatogram trace showing MCP concentration at time t =0; Traces 2, 3 and 4 correspond to chromatograms after 1,2 and 4 hours of MCP degradation respectively

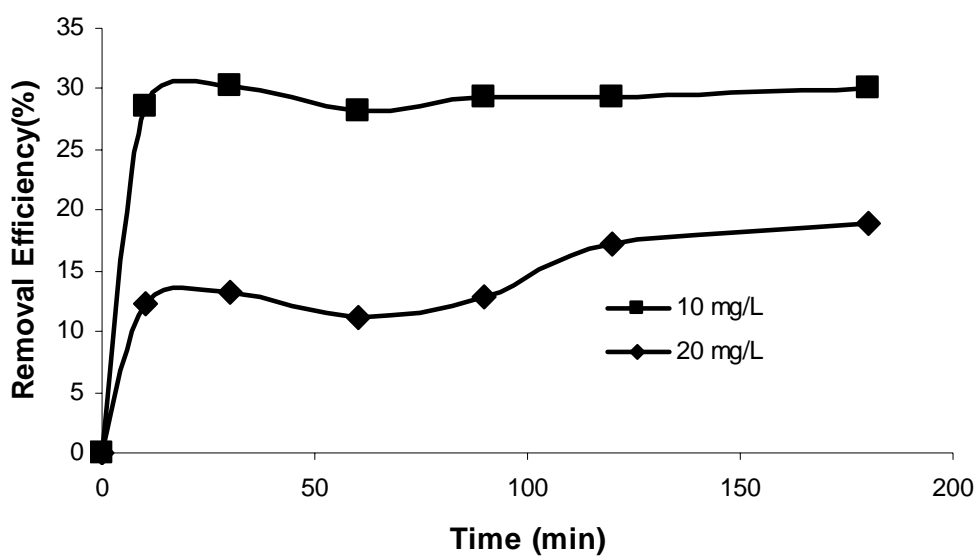


Figure 3 Effect of initial concentration on degradation for monocrotophos (4 g/L TiO₂, 7 pH).

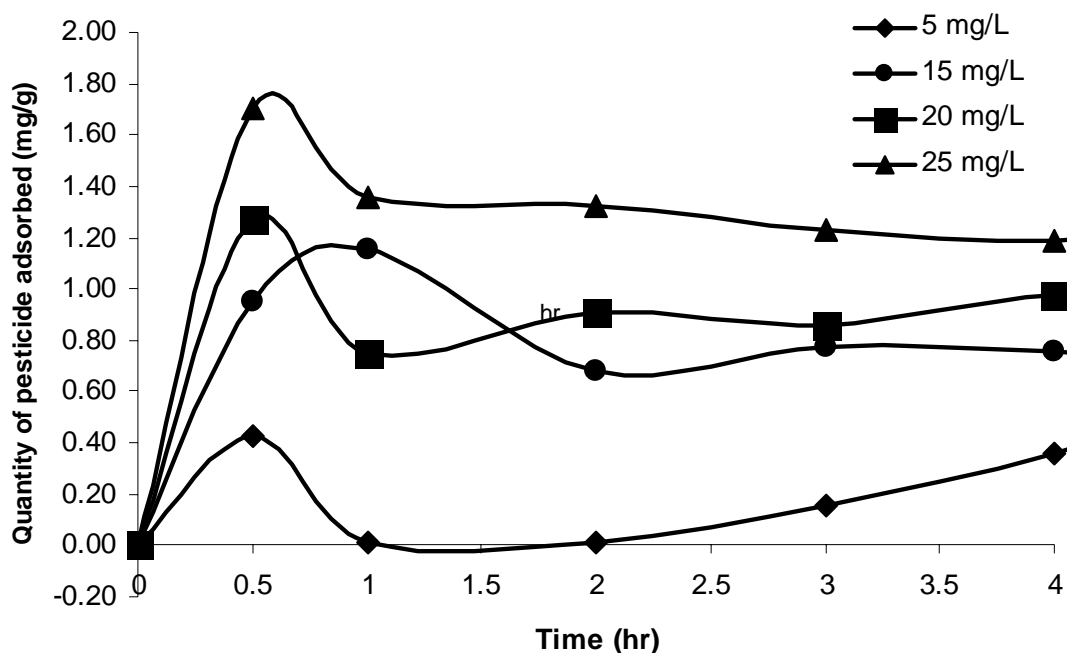


Figure 4 Adsorption behavior of monocrotophos on TiO_2

3.2 Effect of Catalyst Concentration

In heterogeneous catalysis, the catalyst concentration plays an important role in the chemical reactions and has a significant effect on the process efficiency. Since the active sites are proportional to the catalyst concentration, it will affect the degradation significantly. (Ollis and Turchi 1990) Degradation patterns of monocrotophos at different catalyst concentrations of TiO_2 are shown in Figure 3. It was observed that for all the pesticides, the rate of degradation increased when the catalyst concentration was increased from 0.64 to 4 g L^{-1} . However, when the catalyst concentration was further increased to 7 g L^{-1} , the rate of degradation did not show much change compared to catalyst concentration of 4 g L^{-1} . This behavior may be attributed to the shielding effect at higher concentration of catalyst where the suspended TiO_2 reduces the penetration of light to the solution. Wei and Wan, (1991) have also observed increasing and decreasing effects of catalyst concentration on the degradation rate of MCP. Even though more catalyst surface was available for

pesticide adsorption, certain part of the catalyst was not getting exposed to photons.

3.3 Effect of pH

The amphoteric behaviour of titania influences the surface charge of the photocatalyst. The role of pH on the photocatalytic degradation of MCP was studied in the pH range 3–10 at constant MCP concentration of 15 mg L^{-1} at $4 \text{ g L}^{-1} \text{ TiO}_2$. It was observed that the rate of degradation was maximum in the acidic pH and decreased as pH was increased. It was very low at alkaline pH. The results are shown in Figure 4. The same behavior was reported by Shankar et al (2004) where the degradation of monocrotophos was more significant in acidic than in alkaline conditions. pH plays an important role in photocatalytic degradation due to the amphoteric behavior of TiO_2 . Calza and Pelizzetti et al.(2001) have reported that the acid-base behavior of catalyst surface influences the photocatalytic degradation. In photocatalysis, the adsorption of H_2O molecules at surface metal sites is followed by its dissociation to generate OH^- rad-

ical leading to coverage with chemically equivalent metal (Ti) hydroxyl groups (Ti-OH). The following two equilibria are significant for titania.



The zero point charge, pH_{zpc} for Titania is around 6.9 and in acidic pH it is positively charged and in alkaline pH it is negatively charged. The pK_a value of MCP being 4.4, at acidic pH the protonated form predominates while at higher pH it exists in the anion form. Hence the electrostatic interaction between the positively charged surface and protonated

MCP favors adsorption and increases its removal

3.4 MCP Degradation Using Statistical Design of Experiments

The results of MCP degradation using a 2^3 CCD are shown in Table 3. It shows percent degradation corresponding to combined effect of three components in their specified ranges. Degradation varied markedly with the conditions tested, in the range of 11 to 78%. The experimental results suggest that these variables strongly affect the degradation process.

Table 3 Estimated Regression Coefficients for MCP removal efficiency

| Term | Coefficients | St. Dev | T- Value | P- Value |
|-------------------------------|--------------|---------|----------|----------|
| Constant | 53.030 | 4.198 | 12.632 | 0.00 |
| pH | -9.493 | 2.785 | -3.408 | 0.007 |
| Initial conc of pollutant | -8.545 | 2.785 | -3.068 | 0.012 |
| Catalyst | -0.546 | 2.785 | -0.196 | 0.849 |
| pH*pH | 5.347 | 2.712 | -1.972 | 0.077 |
| Pollu. C*Pollu. C | 1.765 | 2.712 | 0.651 | 0.530 |
| Catalyst*Catalyst | -1.143 | 2.712 | -0.422 | 0.682 |
| pH* initial conc of pollutant | 2.559 | 3.639 | 0.703 | 0.498 |
| pH* catalyst | 0.841 | 3.639 | 0.231 | 0.822 |
| Initial conc*catalyst | 1.716 | 3.639 | 0.472 | 0.647 |

3.4.1 Main Effect Plot

The main effects plot for the three variables- pH, initial pesticide concentration and catalyst concentration are shown in Figure 5. It confirms the general trend observed with the preliminary studies. Removal efficiency decreased with increasing MCP concentration; acidic pH condition was favorable for MCP removal; and an optimum value (4gL^{-1}) of catalyst concentration was necessary for maximum removal efficiency.

3.4.2 Statistical Analysis

The results of the experiments were fitted into a second order polynomial regression model as shown in the following equation,

$$Y = 53.030 - 9.493 x_1 - 8.545 x_2 - 0.546 x_3 - 5.347x_1^2 + 1.765x_2^2 - 1.143 x_3^2 + 2.529 x_1x_2 + 0.841 x_1 x_3 + 1.716 x_2 x_3$$

where Y is the response variable, percentage removal of MCP and X_1 , X_2 and X_3 are the coded form of the process parameters as given in Table 1.

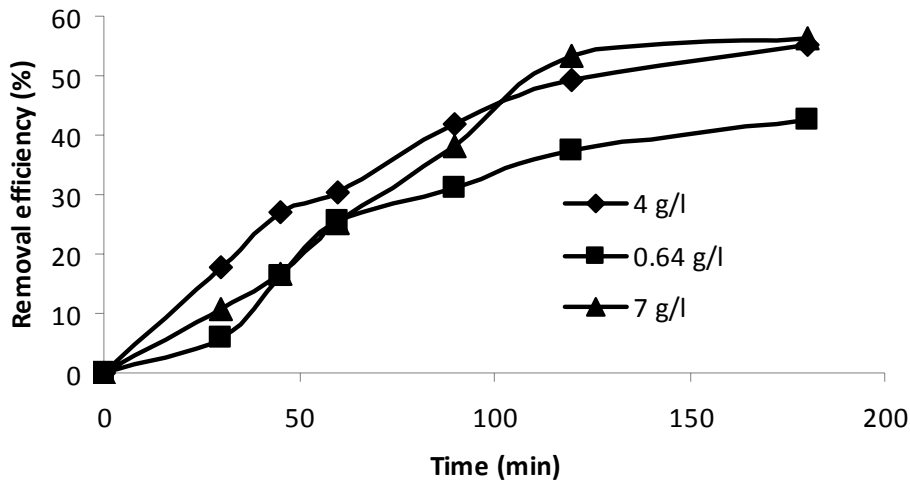


Figure 5 Effect of catalyst concentration on degradation of Monocrotophos (15 mg/L MCP, 7 pH)

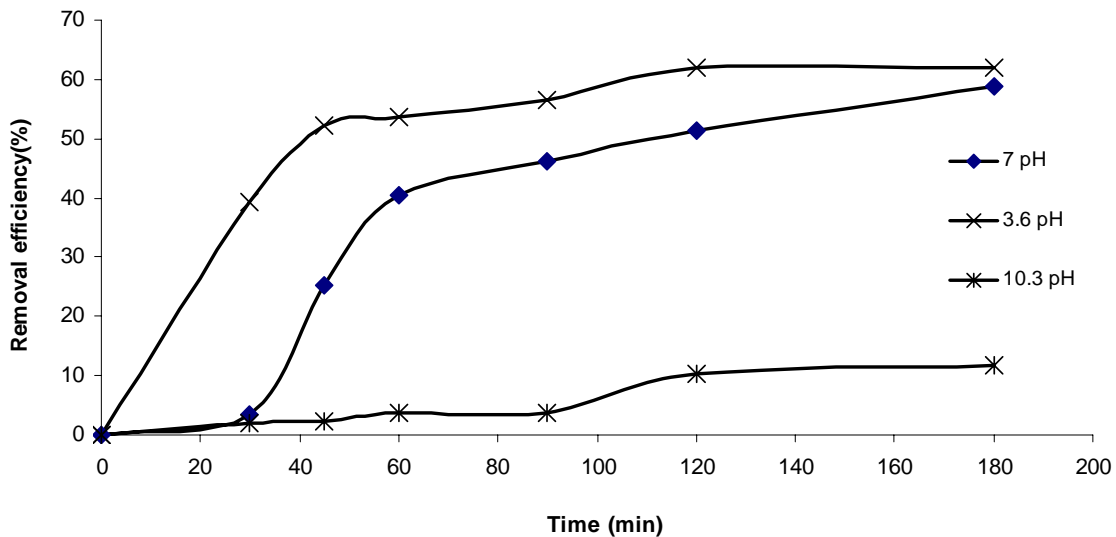


Figure 6 Effect of pH on degradation of Monocrotophos (15 mg/L MCP, 4 g/L TiO₂)

The estimated values of the coefficients are given in Table 3. The significance of the coefficients were tested using the students' *t* test and the probability 'p' value which are also given in Table 3. In general, the larger the magnitude of *t* and smaller the value of *p*, more significant is the corresponding coefficient term (Montgomery, 1991). It was observed that the coefficients of the main effects as well as interaction effects showed relatively higher values of 'p'. The statistical significance of the regression model can be ana-

lysed by ANOVA as given in Table 4. The F values for the model and for each of the response variables were calculated by dividing the mean sum of square due to model variance by that due to error variance. As seen from table 4 the F value for the model is not highly significant this is reflected in the relatively low correlation coefficient R^2 . This indicates that the second order polynomial model does not represent the experimental system very well. This may be due to the fact that the range of variables may not be in the optimal

region. Using the model the optimal conditions were determined as Initial MCP concentration -10 mgL⁻¹, pH - 5.06 and catalyst concentration - 2.69 gL⁻¹. The model predicted optimum removal efficiency at these condi-

tions was 72%. The actual experimental efficiency at these conditions was 79% indicating that the model prediction was reasonably good.

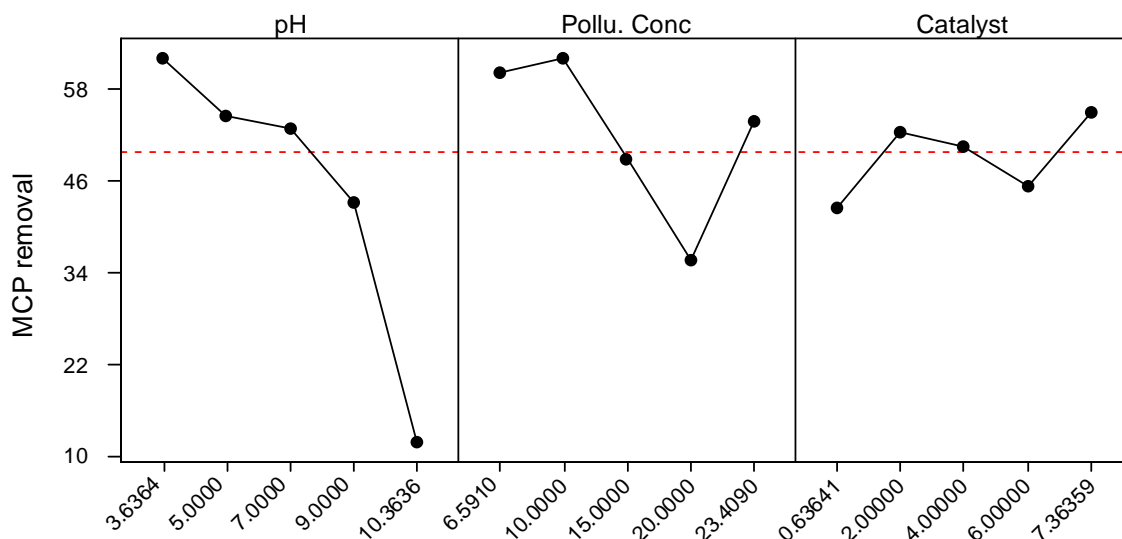


Figure 7 Main effect plots for MCP batch degradation

Table 4 ANOVA for slurry mode degradation of MCP

| | DF | Seq SS | Adj SS | Adj MS | F | P |
|----------------|----|---------|---------|--------|------|-------|
| Regression | 9 | 2812.24 | 2812.24 | 312.47 | 2.95 | 0.054 |
| Linear | 3 | 2232.04 | 2232.04 | 744.01 | 7.02 | 0.008 |
| Square | 3 | 498.60 | 498.60 | 166.20 | 1.57 | 0.258 |
| Interaction | 3 | 81.60 | 81.60 | 27.20 | 0.26 | 0.855 |
| Residual Error | 10 | 1059.59 | 1059.59 | 105.96 | — | — |
| Lack-of-Fit | 5 | 910.56 | 910.56 | 182.11 | 6.11 | 0.034 |
| Pure Error | 5 | 149.03 | 149.03 | 29.81 | — | — |
| Total | 19 | 3871.83 | — | — | — | — |

S = 10.29 R-Sq = 72.6% R-Sq(adj) = 48.0%

4.0 CONCLUSION

The present study clearly demonstrated the applicability of photo catalysis for pesticide degradation in an annular slurry reactor. The pesticide (MCP) degradation was higher at

low pesticide concentration and in acidic pH. The catalyst concentration had both positive impacts up to 4 gL⁻¹ and negative impacts beyond it. Using statistically designed 2³ factorial experiments, a quadratic polynomial model was fitted to the data to predict the de-

gradation efficiency in terms of the parameters and to analyse the significance of the coefficients of the model.

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