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Optimization studies on degradation of monocrotophos in an immobilized bead photo reactor using design of experiment

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ABSTRACT

Pesticides are a major source of environmental concern due to their persistence and health and ecological impacts, particularly in developing countries. Heterogeneous photocatalysis has emerged as a promising technique for their removal from wastewaters. But effective implementation requires the development of efficient and practical photocatalytic systems. A novel photo reactor was developed in this study using TiO_2-coated polymeric beads as floating catalysts which enabled efficient penetration of UV radiation; good mixing and high mass transfer rates. The performance of the immobilised bead photo reactor was evaluated for the removal of an organophosphate pesticide—monocrotophos. Batch studies were carried out using a 2^3 central composite factorial design of experiments, with initial pesticide concentration (1–15 mg/l), initial pH (3.5–10.5), and catalyst loading (2–6 g/l) as process variables. About 50–80% degradation was achieved depending on the levels of initial pesticide concentration, pH, and the amount of catalyst. A quadratic polynomial model was fitted to the experimental removal efficiency and the statistical analysis revealed that the coefficients for the main effects are significant.

Keywords: Factorial design; Immobilised bead photo reactor; Monocrotophos; Photocatalysis; TiO_2

1. Introduction

Contamination of natural waters due to indiscriminate use of pesticides in many parts of the world is now well established. This is particularly important in developing countries, which also have very poor water treatment facilities to provide safe drinking water. The ecotoxicological, carcinogenic, and other human health effects resulting from environmental exposure of pesticides are well researched and documented [1,2]. An emerging concern in recent times is the role of some pesticides as endocrine-disrupting chemicals (EDC), which disrupt the endocrine functions, growth, development, and reproduction of humans and animals. A few adverse effects of EDCs are early maturity, defect in child birth, and impotence [3]. Recent research has highlighted the existence of these chemicals in surface and ground water via point and non-point sources [4], due to their high solubility in water. Several new water and wastewater treatment techniques have been tried for their removal. Neutral solar photo-Fenton degradation of 4-nitrophenol on iron-enriched hybrid montmorillonite-alginate beads (Fe-MABs) was studied by

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Barreca et al. [5]. The effect of montmorillonite clay in alginate gel beads for poly-chlorinated biphenyl isothermal adsorption and its kinetics by the same research group [6]. Martin et al. [7] have compared the pesticide degradation by combined solar photo-Fenton and biological treatment and Augugliaro et al. [8] have studied the heterogeneous photocatalysis and photo electrocatalysis of noxious species for the production of high value chemicals. However, heterogeneous photocatalytic oxidation is emerging to be the most promising technique for the removal of a variety of hazardous contaminants [9].

The major focus of research on photocatalytic degradation of environmental contaminants has been on developing novel photocatalysts. However, the critical issue in application of photocatalysis is designing of efficient reactors. Most of the early photoreactors were based on suspended photocatalysts, which inherently had high degradation efficiencies but had catalyst separation problems. This was overcome by immobilization of photocatalyst, but at the cost of lower efficiency. A new technique using immobilized floating catalyst, facilitates high efficiency with ease of separation. One of the earliest studies on this was by Shifu et al. [10] for the solar photocatalytic degradation of organophosphorus pesticides using floating photocatalyst of TiO_2 coated on hollow glass beads. In the present study, the performance of immobilized bead photo reactor (IBPR) using polymeric beads was evaluated by measuring the degradation of organophosphorous pesticide monocrotophos (MCP) under UV irradiation using statistical design of experiments for optimizing the process parameters.

2. Materials and methods

2.1. Chemicals

The photocatalyst used in this study was titanium dioxide (CDH) pure anatase, BET surface area 15 m^2/g. The pesticide used was monocrotophos (MCP) (technical grade) obtained from local suppliers. All other chemicals used in the experiments were of reagent grade. For HPLC analysis, milli-Q water and acetonitrile (HPLC grade) were used.

2.2. Preparation of immobilized bead catalyst

The polystyrene beads (6 mm) were first cleaned, dried, and mixed with a silicone-based adhesive. These were then mixed with a pre-sonicated slurry of TiO_2. The coated beads were dried in oven for 1 h. The dried beads were stirred in 500 ml of water to remove the loosely bound TiO_2 and dried again for further use.

2.3. Experimental setup of immobilized bead photocatalytic reactor (IBPR)

The schematic of the IBPR experimental setup and a photograph of the IBPR reactor are shown in Fig. 1. The reactor consisted of a rectangular acrylic tank (72 cm × 36 cm × 6 cm) divided into equal sized cells, with a wire mesh placed at the end of each cell to retain the beads within each cell. Aeration through diffusers placed inside each cell helped in maintaining the beads in suspension and also ensured good mixing between the beads and the wastewater. The wastewater was continuously recirculated through the reactor using a peristaltic pump. The flow through cells was designed to give zigzag flow path for the liquid in the reactor. The UV radiation was provided using a parabolic lamp house with three low pressure Hg UV lamps (15 W Philips, Holland).

2.4. Analytical methods

Concentration of residual pesticide in the samples was analyzed by gradient HPLC (Jasco Pu-2089 plus, Japan) with PDA detector using Agilent Eclipse PAH 5 μm Column (10 mm dia. × 150 mm long). Acetonitrile and water (low conductivity) in the ratio of 70:30 was used as mobile phase at a flow rate of 1 ml/min. The pesticide concentration was determined by measuring the absorbance of samples and reading the corresponding concentration from a standard calibration.

2.5. Effect of photolysis on MCP degradation

Effect of photolysis on different concentration of MCP was studied in sunlight with IBPR setup. Residual pesticide concentration was measured using HPLC.

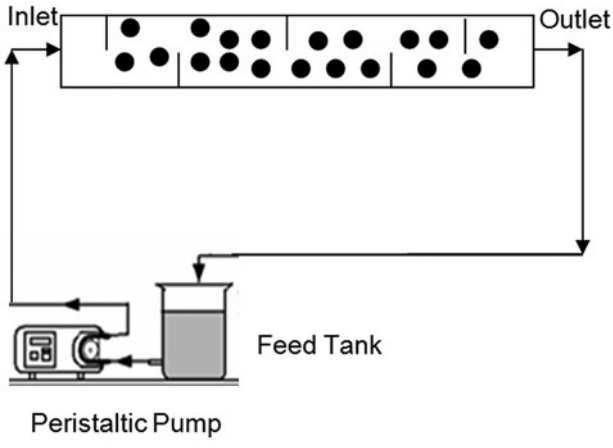

Fig. 1. Schematic representation of IBPR reactor.

2.6. Statistical design of experiments

Statistical design of experiments is a useful method to provide information on the direct effects of not only the main variables but also the effects of interaction between the variables, which cannot be seen in one-factor-at-a time experiments. It also enables formulation of mathematical model to predict the response in terms of main variables and interaction terms and the statistical analysis of data helps in determining the significance of the model fit and the coefficients of the model parameters.

A full factorial design which includes all combination for each factor is a powerful tool for analyzing complex processes [11]. 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 [12]. The ranges of experimental variables are shown in Table 1. Thus, a total of 20 experiments were used as shown in Table 2. The data obtained through the statistically designed experiment was fitted to a second-order polynomial equation (Eq. (1)):

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_i X_i X_j \quad (1)$$

where Y is the response variable. The coefficients of the equation were estimated using a statistical program MINITAB 16 (Minitab Inc, USA). The regression analysis of the data was also performed using the same program. The multiple correlation coefficient R and determination coefficient R^2 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. Results and discussion

3.1. Preliminary batch recirculation studies

Preliminary studies on the photocatalytic degradation of MCP were done by studying the effects of process parameters-initial concentration of the pesticide, pH of the solution and the catalyst concentration, individually. The results are discussed in the following section.

Table 1
Experimental range and levels of variables for MCP degradation

Parameter	$-\alpha$	−1	0	+1	α
Initial pesticide conc. (mg L^{-1})	0.95	3	6	9	11.05
Catalyst conc. (g L^{-1})	0.64	2	4	6	7.36
pH	3.63	5	7	9	10.36

3.2. Effect of photolysis on MCP degradation

Fig. 2 shows the MCP removal with and without immobilized bead photocatalyst (2 g of TiO_2 coated on 200 g of beads) for five hours in sunlight. Direct irradiation (photolysis) could give only 8–12% pesticide removal, while in the presence of the photocatalyst more than 50% removal could be achieved. It was also observed that the rate of removal was lesser at higher pesticide concentration.

3.3. Effect of initial pesticide concentration

The pollutant concentration is an important parameter in wastewater treatment. As oxidation proceeds, the concentration of pesticide and rate of photo degradation are expected to vary with irradiation time. Fig. 3 shows the effect of initial pesticide concentration (in the range of 1–15 mg/l) on the removal of MCP. Nearly 50–90% pesticide removal was obtained depending on pesticide concentration. As pesticide concentration increased the rate of removal decreased. One possible reason for this could be that as pesticide concentration increases more absorption of light radiation occurs on the pesticide in the solution and adsorbed phase, resulting in the reduction of photons reaching the catalyst surface, thus causing a decrease in the amount of hydroxyl and superoxide radicals formed [13]. Hence, the pesticide degradation was found to be reduced at higher concentration. Another possible reason for reduced degradation at higher pesticide concentration could be that the adsorption of pesticide molecule on catalyst surface might also reduce the available surface of catalyst for photon-induced hydroxyl radical generation [14]. Also, the amounts of hydroxyl and super oxide radicals on the catalyst surface do not increase, as intensity of light and irradiation time is constant.

3.4. Effect of pH

The solution pH plays an important role in the aqueous phase photocatalytic reactions. In wastewater treatment, it is also an important operational parameter. The pH of the solution influences adsorption and dissociation of the substrate, catalyst surface charge and oxidation potential of the valence band and other physicochemical properties of the system [15,16].

Table 2
General factorial design for pesticide degradation studies

	Factor 1	Factor 2	Factor 3	
S. no.	pH	Initial conc of pesticide (mg/L)	Catalyst (g/L)	Removal efficiency (%)
1	6	7	7.36	53
2	6	7	4	50
3	9	9	2	35
4	9	5	2	40
5	3	9	6	59
6	6	7	4	51
7	3	5	6	71
8	11.05	7	4	38
9	0.95	7	4	75
10	9	5	6	46
11	6	7	4	53
12	6	10.36	4	40
13	6	7	0.64	43
14	3	9	2	55
15	9	9	6	38
16	6	7	4	51
17	3	5	2	65
18	6	3.64	4	57
19	6	7	4	53
20	6	7	4	50

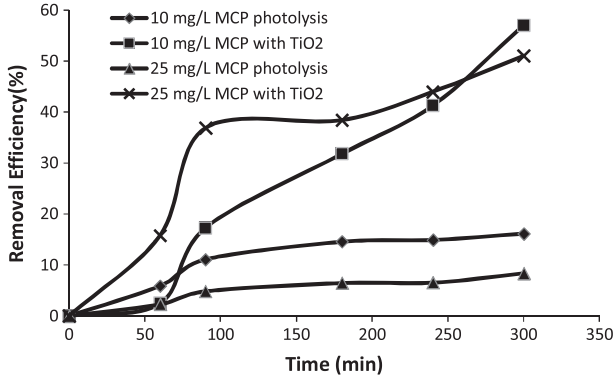

Fig. 2. Comparison of photolysis and photocatalysis on MCP.

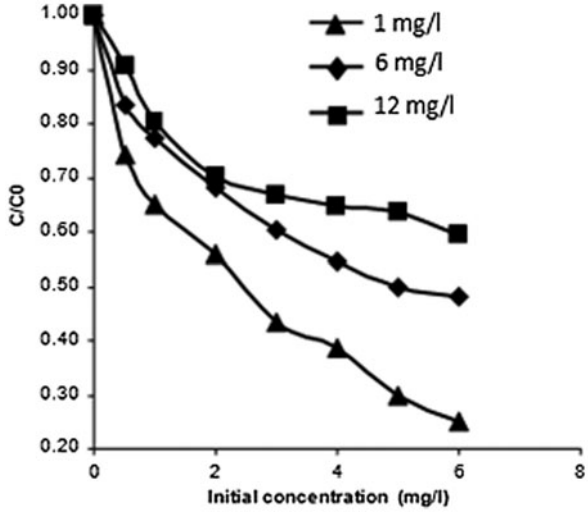

Fig. 3. Effect of initial concentration on MCP degradation.

The effect of pH on the rate of pesticide removal was studied by keeping all other experimental conditions constant and changing the initial pH of the pesticide solution from 3 to 10, and the results are presented in Fig. 4. The rate of degradation increased with decrease in pH. Since the pH_{zpc} of TiO_2 is 6.8, the surface of the catalyst is presumably positively charged and since the pesticide has negatively charged nitrate and phosphate groups, the acidic solution favors the adsorption of pesticide on the catalyst surface or at least brings them closer to it, thus providing enhancement in degradation. Similar results of enhanced photocatalytic degradation of pesticide in acidic pH have been observed in other studies [16,17].

3.5. Effect of catalyst concentration

In conventional immobilization of catalyst on fixed surfaces, it is easy to increase the catalyst concentration which increases the thickness of the catalyst layer.

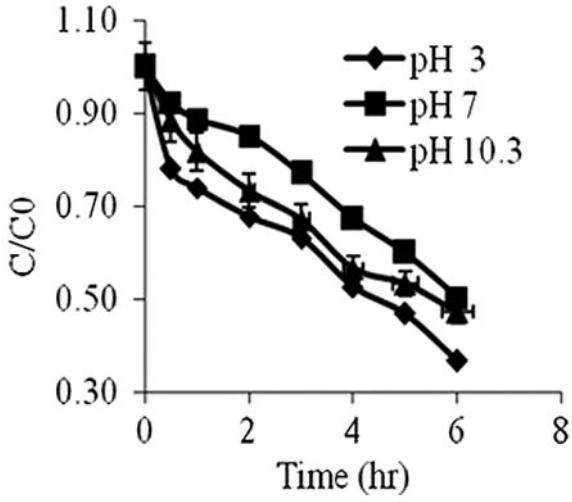

Fig. 4. Effect of pH on MCP degradation.

But in the case of floating catalyst, the catalyst concentration can be increased by either increasing the number of beads which proportionately increases the surface area or by increasing the amount of catalyst coated per bead which increases the catalyst thickness. Hence, both the methods were studied. Catalyst coating thickness for different catalyst load was measured through the analysis of SEM images. Coating thickness measured was varied from 20 to 40 μm. Fig. 5 shows the SEM image of TiO_2-coated beads with different catalyst load per 200 g of beads.

3.5.1. Increasing the surface area by increasing the number of beads

Fig. 6 shows that the photo degradation efficiency of monocrotophos increased rapidly with the increase in the catalyst load from 2 to 4 g/L. Since the beads were prepared at 2 g/200 g beads catalyst load, only a thin coating of the catalyst may be formed on the bead. Hence, an increase in the catalyst concentration by increasing the number of beads results in an increase in the active surface area with concurrent increase in adsorption and reaction rates. However, further increase in number of beads caused a decrease in photo degradation efficiency. Though more catalyst was available, increased number of beads might be obstructing the exposure of inner beads to UV radiation, resulting in reduced photon absorption and hydroxyl radical generation. A similar result on removal of organophosphorus pesticides by photocatalysis using floating catalyst has been reported earlier [18].

3.5.2. Increasing the amount of catalyst/bead

Fig. 7 shows that increasing the catalyst concentration without changing the number of beads also resulted in an increase in the rate of degradation up to 4 g catalyst loading. But at higher catalyst load, the rate of degradation decreased. This is similar to the effect of catalyst concentration observed in slurry systems as well as in fixed, immobilized catalyst system. Since at 2 g/200 beads, only a partial covering of the bead surface was achieved, an increase in catalyst load to 4 g/200 beads, could have resulted in full coverage of the bead surface, thereby increasing the rate of degradation. As the amount of catalyst increases, the number of photons and the number of MCP molecules adsorbed also increased due to an increase in the number of catalyst particles leading to the increase in photocatalytic activity. However, when the support area is completely covered by the catalyst, further increase in catalyst concentration, helps in only increasing the catalyst layer thickness. Since only the surface layer catalyst is active in adsorption and reaction, increasing thickness by increasing catalyst concentration is not likely to increase in pesticide removal.

3.6. Studies on MCP degradation using statistical design of experiments

The results of the experiments on 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 40–80%. The experimental results suggest that these variables strongly affect the degradation process.

The main effects plots for the three variables are shown in Fig. 8. It confirmed the general trend observed in the MCP degradation in the previous sections for effects of individual variables. It was also similar to the results obtained with slurry reactor [19]. Removal efficiency decreased with increasing MCP concentration and acidic pH condition was favorable for MCP removal. The effect of catalyst showed an optimum value 4 g/l beyond which the removal rate did not change.

3.6.1. Statistical analysis

The results of the experiments were fitted into a second-order polynomial regression model as shown in the following equation (Eq. (2)):

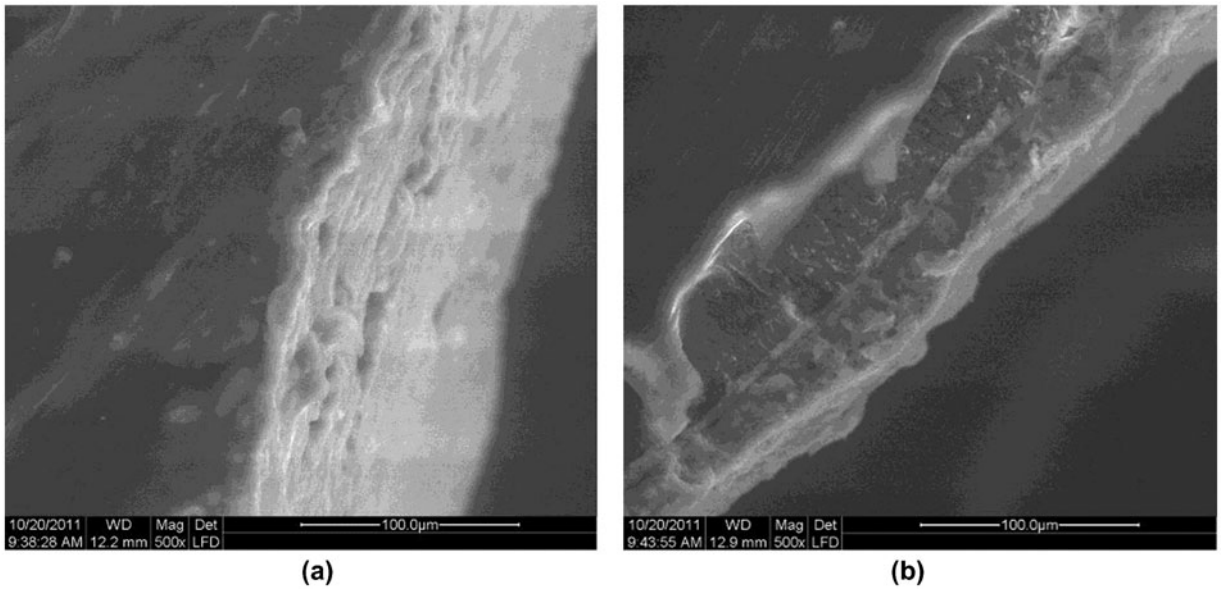

Fig. 5. TiO_2 coating thickness on different catalyst load (a) 2 g of TiO_2 coated on 200 g of beads and (b) 4 g of TiO_2 coated on 200 g of beads.

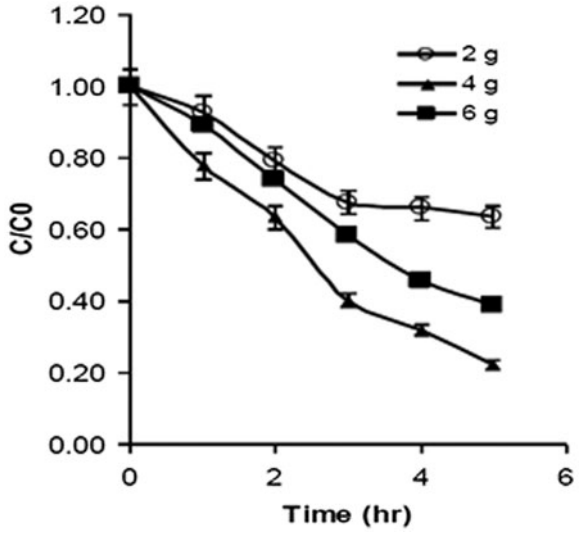

Fig. 6. Effect of increase in catalyst surface area (legend represents the increase in catalyst loading by changing number of beads).

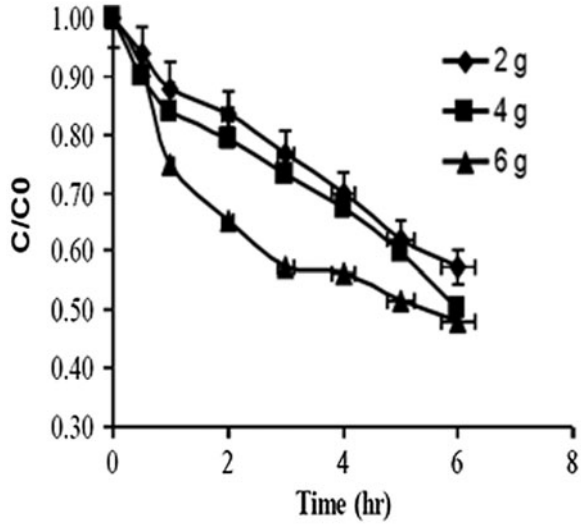

Fig. 7. Effect of increasing the catalyst load on beads.

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

Using the Minitab software the coefficients of the regression model were obtained to give the following equation (Eq. (3)). The significance of the coefficients was evaluated by Student t test for each of the coefficient. The results indicated that:

$$Y = 51.33 - 4.66 X_1 - 11.22 X_2 + 2.62 X_3 + 1.86 X_1^2 - 0.97 X_2^2 - 1.15 X_3^2 + 1.13 X_1 X_2 - 0.62 X_1 X_3 - 0.12 X_2 X_3 \quad (3)$$

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 2. The statistical significance of the regression model was analyzed by ANOVA, as given in Table 4. The F

Table 3
Estimated regression coefficients for IBPR MCP degradation

Term	Coefficients	St. dev	*T*-value	*p*-value
Constant	51.33	0.4597	111.655	0.000
pH	−4.66	0.3050	−15.266	0.000
Initial conc. of pollutant	−11.22	0.3050	−36.785	0.000
Catalyst	2.62	0.3050	8.599	0.000
Initial × initial	1.86	0.2969	6.255	0.000
pH × pH	−0.97	0.2969	−3.271	0.008
Catalyst × Catalyst	−1.15	0.2969	−3.866	0.003
pH × initial conc of pollutant	1.13	0.3985	2.823	0.018
pH × catalyst	−0.62	0.3985	−1.568	0.148
Initial conc × catalyst	−0.12	0.3985	−0.314	0.760

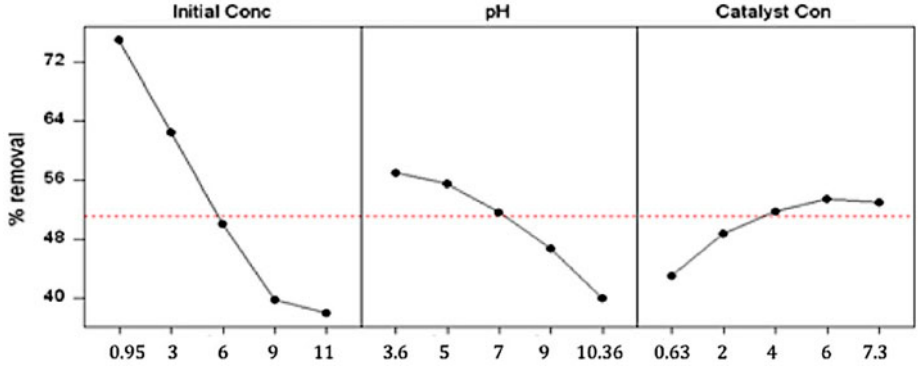

Fig. 8. Main effect plots for MCP batch degradation.

value for the model and for each of the source terms were calculated by dividing the mean sum of square due to model variance by that due to error variance. *F* value (193.62) for the model was highly significant and the same is reflected in the high correlation coefficient $R^2 = 0.98$. This shows that the ranges of variables are in the optimal region. The *F* value for the linear effects of the variables also showed high significance.

The optimal conditions for MCP removal were determined from the model as pesticide concentration = 1 mg/l, catalyst load = 4 g/l, and pH 7. An experiment was conducted at these conditions and the removal efficiency (80%) agreed closely with the predicted efficiency.

3.7. GC–MS analysis of MCP degradation intermediates formed in IBPR

TOC removal studies showed the formation of some stable intermediates, an attempt was made to identify the intermediates using GC–MS. The mass spectrum of monocrotophos is shown in Fig. 9. The GC–MS analysis indicated the presence of several intermediates products in the degradation of monochrotophos. Intermediate 1 was identified as dimethyl methyl phosphate by a library search value with a library search match probability of 89%. The mass spectrum of this compound showed the characteristic ions at $m/z = 79$ and $m/z = 94$ related with dimethyl group and phosphate respectively. Intermediate 2 was identified as trimethyl phosphate by a library search value with a library search match probability of 92%. The mass spectrum of this compound showed the characteristic ions at $m/z = 171$ and $m/z = 75$. Intermediate 3 was identified as methyl phosphate with a library search match probability of 79%. The mass spectrum of this compound characteristic ions at $m/z = 47$ and $m/z = 76$. It has been reported in the literature that the photocatalytic degradation of organophosphate pesticides takes place first in ester group that has strong acidity. Then the pesticide is degraded into trimethyl phosphate ester, formic acid, acetic acid, and some small molecule organics. Trimethyl phosphate ester is photocatalytically degraded directly into phosphates and formic acid.

Table 4
ANOVA for IBPR degradation of MCP

Source	DF	Seq. SS	Adj. SS	Adj. MS	*F*	*p*
Regression	9	2,213.85	2,213.85	245.983	193.62	0.000
Linear	3	2,109.20	2,109.20	703.065	553.39	0.000
Square	3	91.27	91.27	30.425	23.95	0.000
Interaction	3	13.38	13.38	4.458	3.51	0.057
Residual error	10	12.70	12.70	1.270		
Lack-of-fit	5	3.37	3.37	0.674	0.36	0.856
Pure error	5	9.33	9.33	1.867		
Total	19	2,226.55				

Notes: S = 1.127; R-Sq = 99.4%; R-Sq(adj.) = 98.9%.

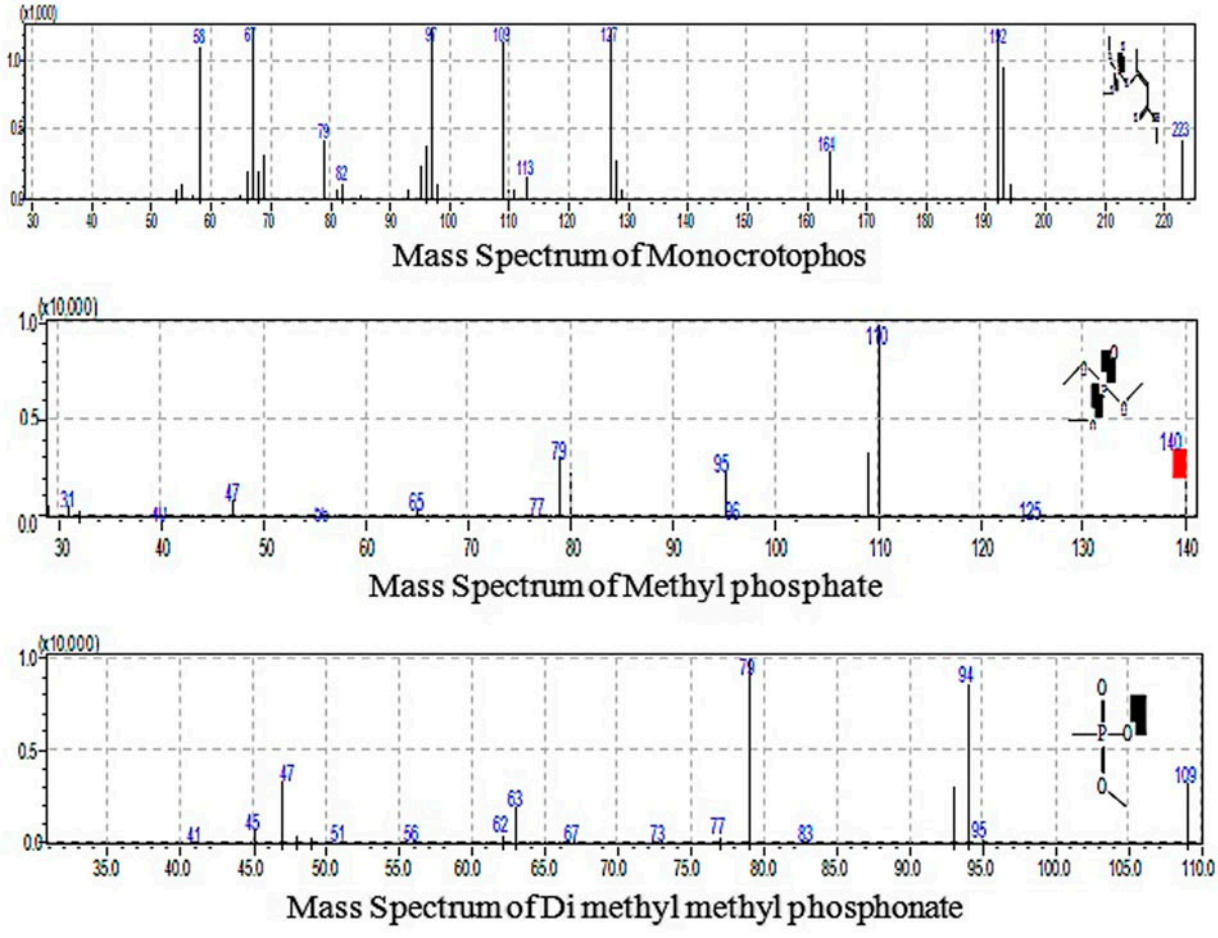

Fig. 9. GC–MS analysis of MCP and its intermediate degradation products formed in IBPR.

4. Conclusion

The present study clearly demonstrated the applicability of photocatalysis for pesticide degradation in an IBPR. The pesticide (MCP) degradation was higher at low pesticide concentration and in acidic pH. The catalyst concentration had both positive impacts up to 4 g/L and negative impacts beyond it. Using statistically designed 2^3 factorial experiments, a quadratic

polynomial model was fitted to the data to predict the degradation efficiency in terms of the parameters and to analyze the significance of the coefficients of the model. GC–MS analysis shows the lower molecular weight intermediate degradation products formed during the degradation of MCP.

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