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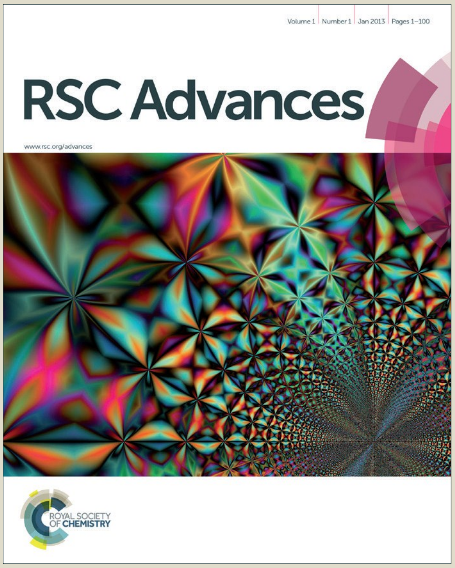

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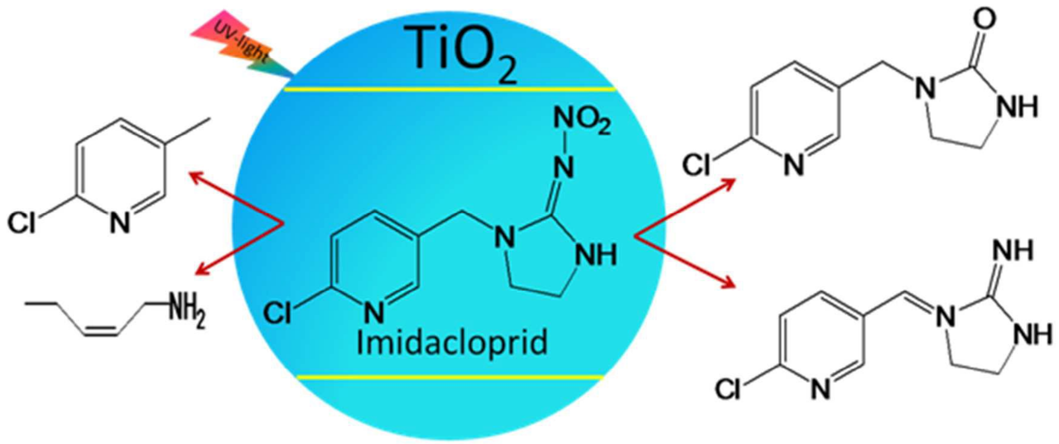
Graphical Abstract



Title: Photocatalytic degradation of imidacloprid in soil: Application of response surface methodology for optimization of parameters

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Abstract

The photocatalytic mineralization of imidacloprid to inorganic ions and various intermediates formation using TiO_2 as photocatalyst in soil was investigated under UV-light. Various parameters viz., catalyst concentration, soil depth & pH, intensity of light and initial concentration of IMI were optimised theoretically by using central composite design based on response surface methodology and were correlated with the experimental results. The statistical analysis from the modelling results indicated that degradation efficiency of IMI was affected by depth of soil, intensity of light also, but effect of pH and initial concentration of imidacloprid were more dominant. The optimum conditions obtained for maximum degradation of imidacloprid were at pH = 3; intensity of UV light =30Wm^{-2}; soil depth= 0.2cm and initial concentration of imidacloprid =10 mg kg^{-1} of soil. Under these optimum conditions, the highest degradation of 82% was achieved after 18 h of UV light irradiation. The identification of various photoproduced intermediates of IMI by LC-MS analysis revealed its degradation, whereas the increase in formation of inorganic ions with time of UV light irradiation confirms its mineralization.

Keywords: Soil, TiO_2, Photocatalytic degradation, Response Surface Methodology, Mineralization, Mechanism

1 Introduction

Soil, an ultimate sink for accumulation of applied pesticide have attracted the current research interest in-terms of analysing leaching behaviour, formation of intermediate products and role of parameters affecting degradation of pesticides. Upon contact of pesticide with soil, binding between them takes place, with the extent being dependent on the nature, composition, texture, organic matter, pH, cation exchange capacity, electrical conductance and moisture of the soil (1). Adsorption of pesticide with soil is a crucial factor, as it is well known to influence (2) their persistency, degradation and fate in the soil. For instance, adsorption and desorption process were reported (3) to determine the mobility of pesticides and were found to be influenced by physico-chemical properties of soil. Some studies have shown that organic matter affects binding of pesticide molecules with soil (4) and is reported as a major controller component in the sorption, transformation, and transport of many organic pollutants in soil (5).

Imidacloprid (IMI), belonging to neonicotinoids family of insecticides, effective on insects that are resistant to carbamates, organophosphates and pyrethroids, has been admitted from past two decades over 120 crops worldwide. This insecticide because of its high water solubility, leaching behaviour and half-life has contaminated the soil and water reservoirs nearby the agricultural fields, and is of concern for the environment (6). Its natural degradation is slow in soil under natural conditions, decomposes sometime more toxic and persistent intermediates than IMI itself. Therefore, efforts have been made to degrade and study the formation of metabolites of IMI biologically (7-11) in soil and broth. The degradation of IMI has also been studied photocatalytically in water (12, 13) using TiO_2 as photocatalyst. The available reports reveal that approx 95% degradation of IMI could be done by photocatalysis in water (14). No studies have been reported on photocatalytic degradation of IMI in soil however for other molecules such diuron (15), PNP and polycyclic aromatic hydrocarbons (16, 17), the same process is well reported. Therefore, using TiO_2 as a photocatalyst in soil could be useful for mineralization of

IMI, and seems to be unexplored. Hence, degradation of IMI using commercially available Degussa P25-TiO_2 as photocatalyst, under UV-light irradiation in soil has been studied.

Generally, Single-variable-at-a-time (SVAT) method is used to study photocatalytic process (18,19), however it suffers from some disadvantages viz., time consumption, incapability to account for interactions between different variables and hence in predicting the optimum conditions (20). On the contrary, central composite design (CCD) based on response surface methodology (RSM) is found to be more convenient, as it provide the good correlation between the various parameters in much less time (21,22). Although, this approach has been employed for the degradation of various pollutants in air and water (23-28), yet much less work has been carried out using the same in soil.

Hence in this study, various parameters such as intensity of light, pH, initial concentration of IMI and depth of soil affecting the degradation of IMI were optimized using CCD based on RSM. The predicted response values from RSM were compared with experimental photo-catalytic degradation efficiency of IMI. Under these optimized parameters degradation of IMI was experimentally studied using HPLC along with identification of metabolites formed by LC-MS technique, and the fate of heteroatom (N,O, Cl) present were studied by ion chromatography.

2 Experimental Methods

2.1 Materials

Imidacloprid (99%) and TiO_2 (Degussa P25, average particle size of 30-50 nm, anatase: rutile :: 80:20) were obtained as gift samples from Bayer crop science India Ltd., Mumbai and Evonik Industries, respectively. Acetonitrile (HPLC grade), de-ionized water, H_2SO_4 and NaOH were obtained from Loba Chemi, India.

2.2 Experimental procedures

The soil samples from surface (0-10 cm) collected from Thapar university campus, Patiala (Punjab), India, were firstly air dried and passed through 1 mm sieve. Sieved soil samples were autoclaved (121°C, 3 × 30 min) and stored in the dark. Adsorption and photodegradation studies (with and without TiO_2) were performed in UV reactor equipped with six UV lamps (Phillips, 20W) with such an arrangement that height of the soil samples with respect to UV light can be varied (*Electronic Supplementary Information (ESI) fig.1*) as reported previously (29) by our group. The internal temperature of the chamber was maintained by using exhaust fan. The pH (3, 7 and 11) of the soil was maintained by using 0.1 N HCl/NaOH and temperature was maintained by circulating the water below soil samples petriplates. The soil samples were spiked to 50 mg kg^{-1} of the soil using acetonitrile solution of IMI and known amount of soil (5 g) was evenly spread on glass petriplates (90 mm of diameter), forming a layer of 0.2 cm estimated from soil bulk density and petriplate area. Moreover, the soil samples spiked with IMI have been irradiated without TiO_2 and hereafter termed as photolysis.

Further soil samples (5g) from irradiated and non-irradiated experiments were extracted by stirring with acetonitrile for in 50 ml beaker followed by sonication in an ultrasonic water bath (EN 60 US, tank size 12’’×6”×6” , 100W, 33±3 KHz). After extraction solution was separated from the soil by centrifugation and washed with acetonitrile. The extract solution thus obtained was filtered (0.22 µm Millipore syringe filter) and analysed by using UV–VIS spectrophotometer (λ_{max}= 270 nm, Hitachi V-500 UV/VIS, Japan).

The photoproducts formed during degradation of IMI were quantitatively analysed by LC-MS technique using Waters Alliance 2795 LC-MS (Waters, UK) linked with a Micromass Q-Tof system equipped with a Shimadzu column C18 (250 × 4.6 mm, 5 µm), at 20°C. The acidified (0.1% acetic acid) mobile phase (acetonitrile: water:: 50:50) was isocratically flow at a rate of

0.3ml/min. Mass analysis was performed with a Z-spray source for positive electrospray ionization at using multiplereaction monitoring (MRM) scan mode in a range of 50-300 m/z. The source and probe were isothermally kept at 140 and 250 ^{o}C, respectively and N_2 (1 ml/min) was used as source of nebulisation. The sample injection volume for LC-MS was 10 µl.

Quantification of inorganic anions (nitrate, nitrite and chloride) produced has been estimated by injecting 100 µl of the sample into Ion chromatograph equipped with a Waters 501pump, a Waters 431 conductivity detector, and ion pack (50 mm × 4.6 mm, Metrhom) column using methanol: water :: 60:40 as mobile phase @ 0.6 ml min^{-1}.

2.3 Experimental design and data analysis

Parameters such as UV light intensity, initial conc. of IMI, pH, TiO_2 catalyst dose, reactor configuration etc., are some of the factors responsible for photocatalytic oxidation (30). However, it is very difficult to carry out an experimental design including abovementioned factors because of large number of experiments (31). Therefore, four variables pH, initial concentration of IMI, intensity of UV light and depth of soil were investigated which includes all the possible combinations for each factor. This multivariable experimental design was done according to CCD based on RSM and the photocatalytic degradation efficiency was selected as response. Analysis of experimental data was supported by Design-Expert Software (trial version 9.0.3.1, Stat-Ease, Inc., MN, USA) (21, 32, 33). These variables were firstly converted to dimensionless ones (A,B,C,D) with coded values at levels:- -α,1,0,+1,+α as shown in *ESI*- table1. These five levels depicting controlling factors are 3-11 for pH values (A); 10-30 Wm^{-2} for intensity of light (B); 5- 25 g amount of soil (C) in petriplates of fixed diameter of 90 mm (correspond to soil depth ranges from 0.2-1cm respectively); 10-90 mg of IMI kg^{-1} of soil for initial concentration of IMI (D) in soil. The 30 combinations obtained by software were experimentally performed in the present study and shown in table1.

3 Result and Discussions

3.1 Preliminary experiments

Preliminary experiments were carried out in order to evaluate the photolysis and adsorption of IMI in soil. It was observed that change in the concentration of IMI was not significant when kept under dark for 18 h ascribed to its adsorption in soil. As pH has significant effect on adsorption of pollutants, therefore adsorption studies for IMI on soil at different pH (3, 7 and 11) were performed (Fig.1a). The adsorption of IMI in soil was ~5% at pH = 11 and it increases up to ~9% at pH = 3. This indicates proto-nation of imdazole ring and is found be in good agreement with the work of Jodeh et al. (34) where proto-nation of imidacloprid reported to be a cause for decrease in its sorption in alkaline silty clay soil. Moreover, photolysis of IMI in soil at optimum adsorption pH was carried out, showing no notable change in its amount even after 18 h of UV-light irradiation. This clearly depicts the stability of IMI molecule and is accordance of reports (12) where its half life is reported to be 40-60 days. However, when soil having IMI was irradiated with UV-light in presence of TiO_2 (0.1- 0.5g Kg^{-1}) the degradation was perceived and found to be dependent upon its amount (Fig.1b). It was observed that degradation increases with increase in photocatalyst doses upto an amount of 0.3 g kg^{-1} and thereafter it decreases. Generally, increase in the amount of catalyst actually increases the number of active sites on the photocatalyst surface, thus causing an increase in the number of •OH radicals which actually participate in IMI degradation. But with further increase in amount of TiO_2, the light penetration declines causing decrease in formation of excited charge carriers and hence oxidative hydroxyl and superoxide radicals (35, 36) therefore there is decrease in degradation rate.

Thus 0.3g TiO_2 per kg of the soil was found to be optimum which was further used for optimizing other four experimental parameters (A,B,C,D).

3.2 Response surface modelling and data analysis

The experimental design concludes 30 experiments and the results came from experimental data are presented in table 1. A theoretical co-relation between these parameters could be expressed as follows:

R = +64.69562 -1.20421 pH + 1.41174 Intensity- 0.36298 soil + 0.010786 conc.-0.098242 pH Intensity-0.11836 pH soil -0.042773 pH conc.- 0.024414 soil Intensity-0.014629 Intensity conc.+ 2.30469E-003 soil conc. +6.67969E-003 pH Intensity soil+ 2.48047 E-003 pH Intensity conc. + 1.52344E-003 pH soil conc. -8.98438E- 005 Intensity soil conc. -7.42188E -005 pH Intensity soil conc.

In the above expression, R is the response variable for degradation efficiency of imidacloprid. Adequacy and significance of the model (response surface reduced quadratic model) was checked by applying ANNOVA which is one of the most important test for the evaluation of data. Thus from table 2, the probability value for A and D are very low (<0.0001) as compared to B and C. This shows that variables A (pH) and D (concentration of IMI) have much significant effect than B (intensity of light) and C (depth of soil) in the degradation of IMI. The ANNOVA results showed that the factors with very low value of probability have more significant effect on the degradation as compared to the factors having high value of probability. Additionally, adequacy of selected model with real system was confirmed by analyzing the correlation between observed and predicted values. The parity between experimental and predicted values are given in Figure 2a where the experimental data has been reasonably fitted well within ±10 %.The response factor of calculated residual values were plotted and shown in fig 2b which depicts that all data points lie close to straight line and within 95% confidence intervals line with mean values near zero. The plot of internally studentized residuals vs predicted values (*ESI-fig.2)* depicted that points are randomly scattered and values lie within the same range (-3 to +3).

Moreover, the 3-dimensional response surface plots (Fig. 3, 4 and 5) and two dimensional contours (*ESI-fig.3, 4 & 5*) further confirms that highest degradation (82%) could be achieved under the optimized parameters. Figure 3 reveals the significant impact of soil pH and initial IMI concentration on degradation of IMI. It can be seen that in acidic soil and lower concentration of IMI, the degradation is maximum. This could be accredited to the fact that with decrease in pH, the TiO_2 surface become cationic (37), causing increase in attractive interaction between the O atom (partially negative) of resonance stabilized (*ESI- fig.6*) $-NO_2$ group in IMI. Consequently, adsorption of IMI increases favouring more number of IMI molecules to be present at the interface of TiO_2 and hence the degradation efficiency. However, at pH= 9-11, reduction in degradation efficiency (50% to 15%) could be ascribed to the protonation of imidazole ring as revealed by the dark adsorption studies. At low concentration of IMI, the degradation is faster than at high concentration of IMI. With the increase in concentration of IMI the screening effect dominates and prevents the penetration of the light and hence reduction in the generation of $OH^{\cdot}$ radicals on the catalyst surface (38). The degradation of IMI is further found to be affected by soil depth (Fig. 4 & 5) and intensity of light. Increase in the soil depth (0.2-1cm) causes decrease in degradation efficiency. This is because the sunlight cannot reach deep inside the soil and the necessary conditions for the photocatalytic degradation are absent in this part of soil hence degradation decreases as the soil layer becomes thicker (39,40). The degradation efficiency was found to increase with increase in light intensity. This could be credited to more availability of photons for excitation of valance band electrons leading to predominate formation of electron-hole pair and thereby diminishing the charge recombination process (41-43). However, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the degradation of the IMI on soil surfaces.

Experiments which were carried out, yielded maximum degradation of 83%, in agreement with the predicted response of 86% verified the validity of optimal point, indicating that CCD could be effectively used to optimize photocatalytic degradation of pollutants.

3.3 Degradation kinetics under optimum conditions

The photocatalytic oxidation kinetics of many organic compounds is fitted to Langmuir–Hinshelwood (L–H) model as :

$$-\frac{dC}{dt} = \frac{kKC}{1+KC}$$

Where, k is the reaction rate constant, K is the equilibrium adsorption constant, C the substrate concentration at any time t (44). In case of low concentration of reacting substrate this equation simplifies to apparent first order kinetics:

$$-\ln(C/Co) = k_r K \ t = kt$$

The plot for –ln(C/Co) vs. time of irradiation, found to be a straight line with slope (k) 0.0957 min^{-1} as shown in Fig. 6.

3.4 Degradation reaction mechanism under optimized conditions

A clear contrast has been found for the LC chromatograms obtained for the photolysis and photodegradation of IMI (*ESI-fig. 7*). It can be clearly seen that peak height of the IMI after 18 h of its photolysis is comparatively higher than that found for the sample after photodegradation. Moreover, some new peaks at R_t = 1.6, 1.9, 2.3 and 2.5 min have appeared for the sample after photodegradation while only peak at R_t = 1.6 min was found after photolysis sample. The various intermediate products were identified by LC-MS analysis (*ESI-fig.8*) as compound B (R_t = 1.95min), C (R_t =1.63 min), D (R_t =2.09 min) and E (R_t =3.32 min). The formation of these identified intermediates could be explained on the basis of proposed pathway (Fig. 7) suggesting various possible attack positions by the hydroxyl radical at IMI.

The preliminary attack of hydroxyl radicals at N-N in IMI expected to yield compound D which further degrade to compound E. The hydrolysis of IMI could result in the formation of intermediate compound B, which degraded to compound C via attack of hydroxyl radicals and is reported to be an intermediate product of IMI photooxidation. The formation of these identified intermediates during photolysis and photodegradation is in accordance to the previous reports (45) concerning the same in aqueous media.

Investigation for the fate of heteroatoms showed that the amount of inorganic ions formed after 18h of photodegradation is notably higher than that found after photolysis of IMI (Fig. 8), indication less mineralization in case of photolysis. The increases in formation of inorganic ions, with time of UV-light irradiation further confirm the mineralization of IMI, during its photodegradation. The formulated (eq.1) balanced stoichiometric chemical equation for nitrate, nitrite and chloride ions during the photodegradation of IMI in present study found to deviate from the expected balance equation (eq.2) after complete its degradation. The existence of indentified intermediates composing the heteroatoms accounts for the incomplete mineralization. The increase in the amount of nitrate ion formation with irradiation time is probably due to mineralization of the imidazole or pyridine-substituted ring(s). These results are in correlation with a previous study (46, 47) for the dissipation of cyrpoconazole and fenhexamid, where the nitrogen atoms present in the triazole moiety were found to decompose to nitrate and ammonium ions.

$$C_9H_{10}N_5O_2Cl + (3/2)\ O_2 \xrightarrow[hv\ (18\ h)]{TiO_2} 0.10\ NO_2^- + 0.63\ NO_3^- + 0.57\ Cl^- + \text{Intermediates}$$

.....eq. 1

–

$$C_9H_{10}N_5O_2Cl + \frac{33}{2} O_2 \longrightarrow 9CO_2 + 5NO_3^- + Cl^- + 6H^+ + 2H_2O$$

.....eq. 2

4 Conclusions

Photocatalytic degradation of IMI could be effectively done using TiO_2 as photocatalyst in soil surfaces. Present study showed the dependence of degradation of IMI on the pH, intensity of light, depth of soil and initial concentration of IMI. The abovementioned parameters were firstly optimized using CCD in RSM supported by Design-Expert Software and the number of experiments came from software were selected and experimentally performed to find out the photocatalytic degradation efficiency. Therefore, under the optimized conditions, mineralization of IMI to inorganic ions and various metabolites could be achieved to overcome the problem of persistence of IMI in soil.

Acknowledgements

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Tables and Figure Captions:

Table1. Experimental and calculated values for degradation of imidacloprid during photocatalytic process.

Table 2. Response surface model regression coefficients and P-value for responses.

Fig. 1 (a) Adsorption studies of IMI at different pH on soil surfaces and (b) Effect of TiO_2 concentration on degradation of imidacloprid (50 mg Kg^{-1} of soil) after 18 h of UV light irradiation (20 Wm^{-2}) in soil (pH = 7, depth 0.2 cm).

Fig. 2 (a) Experimental and calculated values for degradation of imidacloprid and (b) internally studentized residuals plot during photocatalytic process.

Fig. 3 Response surface graph for the interaction between pH and initial imidacloprid concentration at fixed depth of soil (0. 2cm) and light intensity 30 Wm^{-2}.

Fig. 4 Response surface graph for the interaction between light intensity and initial imidacloprid concentration at fixed depth of soil (0.2 cm) and pH= 3.

Fig. 5 Response surface graph for the interaction between depth of soil and initial imidacloprid concentration at fixed intensity of light 30 Wm^{-2} and pH = 3.

Fig. 6 Kinetics and mineralization profiles of imidacloprid at optimum conditions in soil (initial IMI conc. 50mg kg^{-1}, pH=3, intensity of light 30 Wm^{-2}). Inset: Time course UV-Visible spectrum for degradation of imidacloprid.

Fig. 7 Proposed pathway for the degradation of imidacloprid.

Fig. 8 Evolution of inorganic ions during photocatalytic degradation of imidacloprid.

Figures

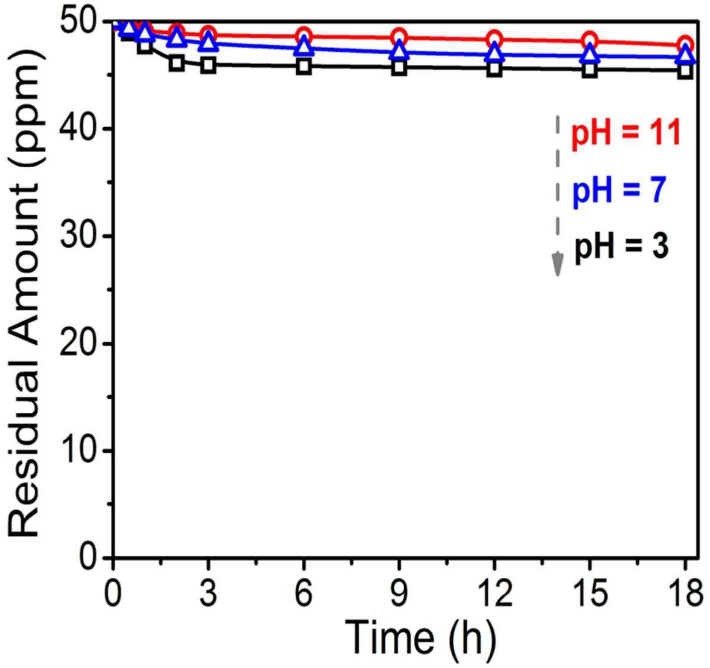


Figure 1a

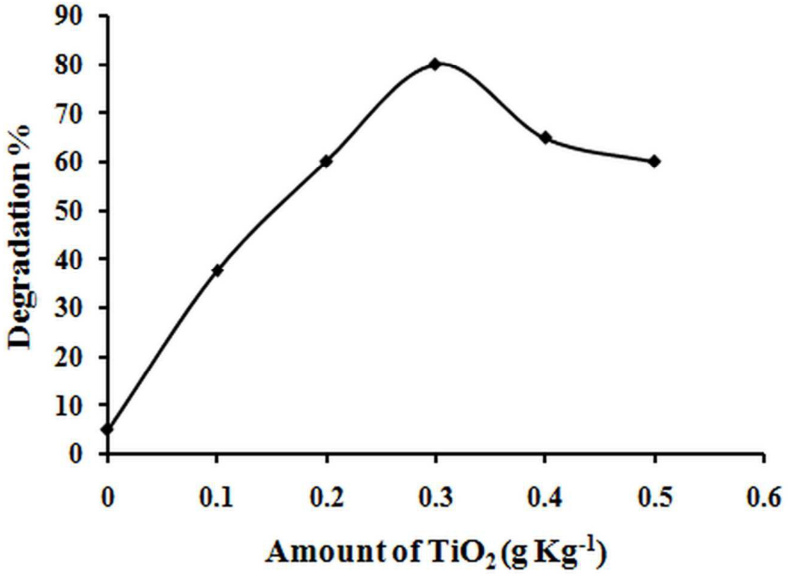


Figure 1b

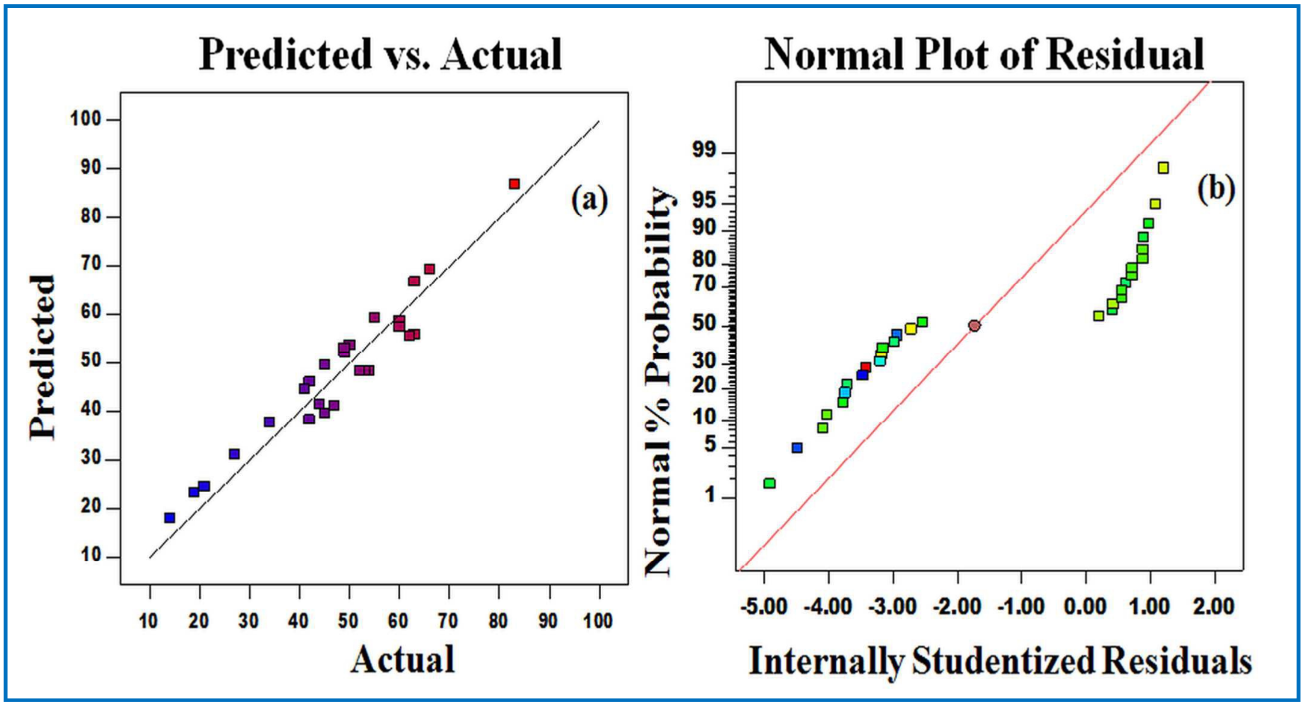

Predicted vs. Actual
(a)
Predicted
100
90
80
70
60
50
40
30
20
10
Actual
10 20 30 40 50 60 70 80 90 100
Normal Plot of Residual
(b)
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-5.00 -4.00 -3.00 -2.00 -1.00 0.00 1.00 2.00
Internally Studentized Residuals

Figure 2a & 2b

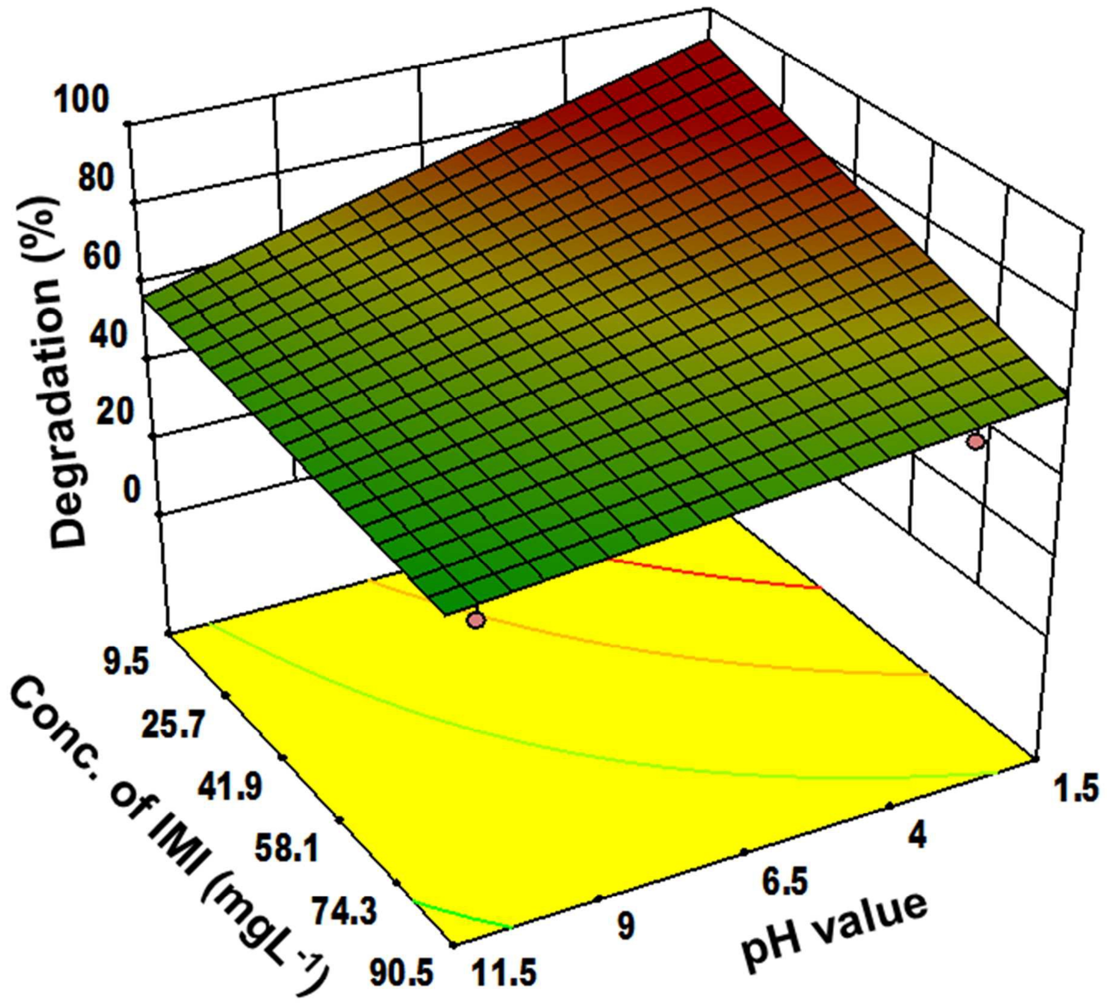

Degradation (%)
100
80
60
40
20
0
Conc. of IMI (mgL⁻¹)
9.5
25.7
41.9
58.1
74.3
90.5
pH value
11.5
9
6.5
4
1.5

Figure3.

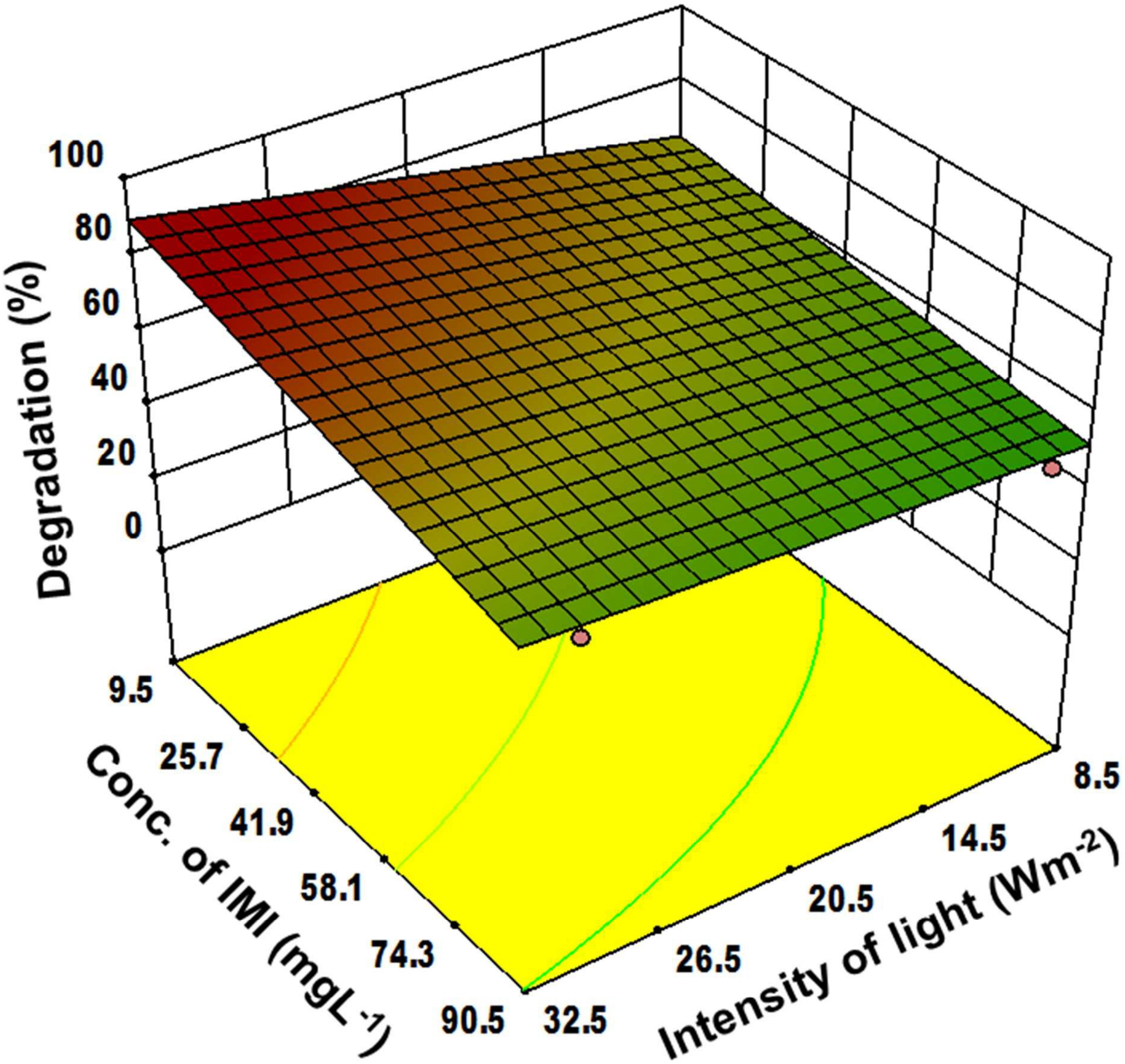

Degradation (%)
100
80
60
40
20
0
Conc. of IMI (mgL-1)
9.5
25.7
41.9
58.1
74.3
90.5
Intensity of light (Wm-2)
32.5
26.5
20.5
14.5
8.5

Figure 4

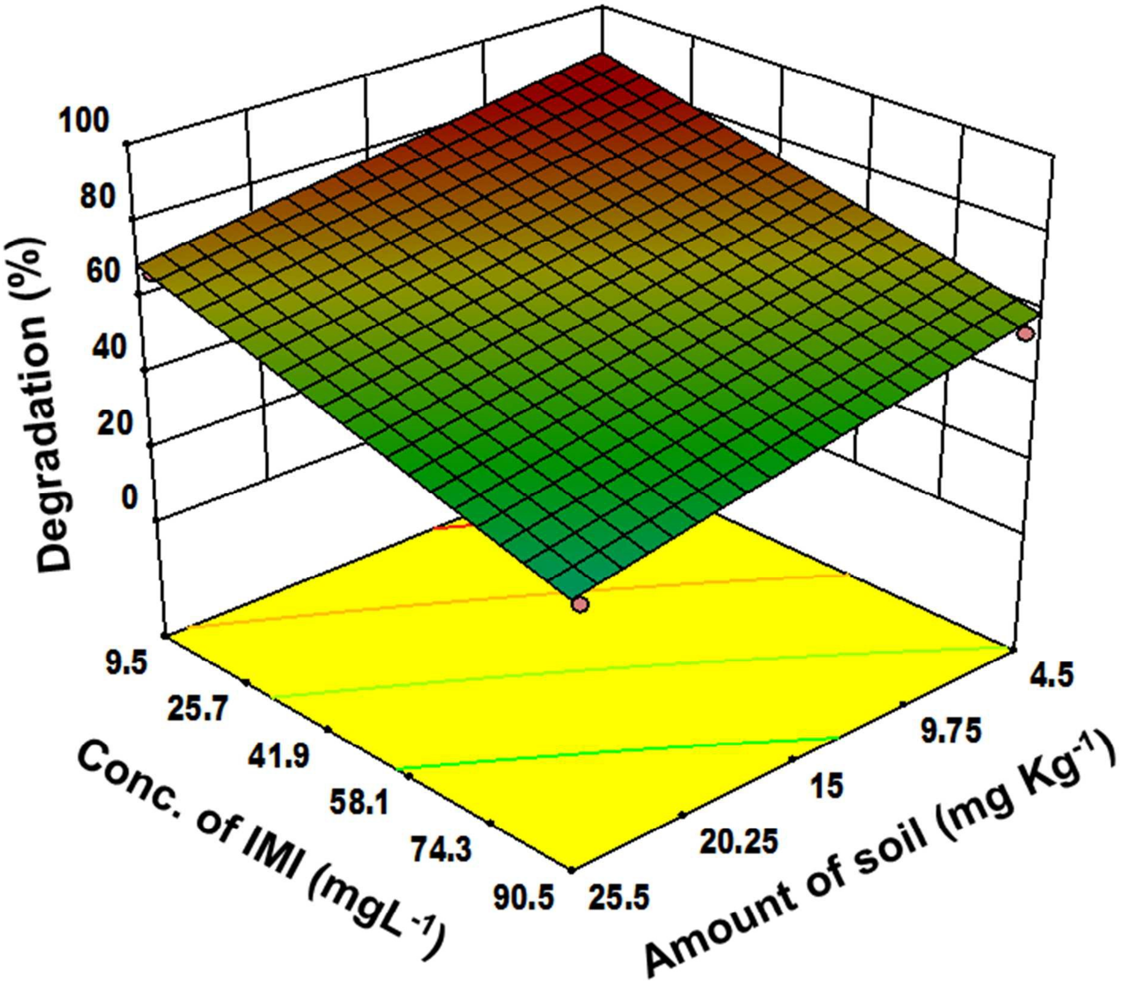

Degradation (%)
100
80
60
40
20
0
Conc. of IMI (mgL-1)
9.5
25.7
41.9
58.1
74.3
90.5
Amount of soil (mg Kg-1)
4.5
9.75
15
20.25
25.5

Figure 5

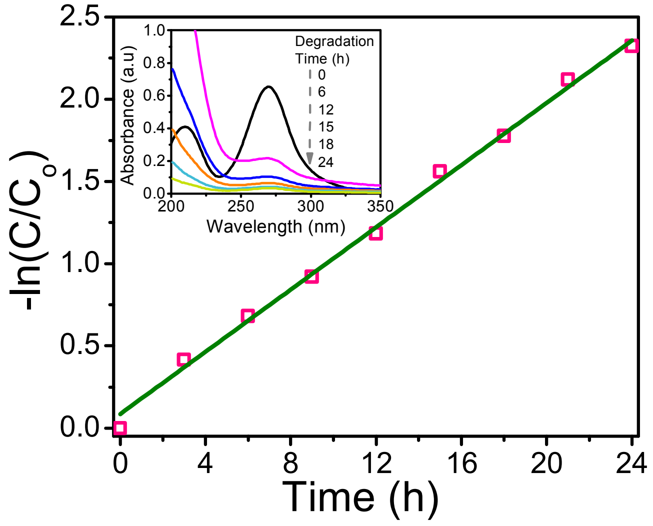


Figure 6

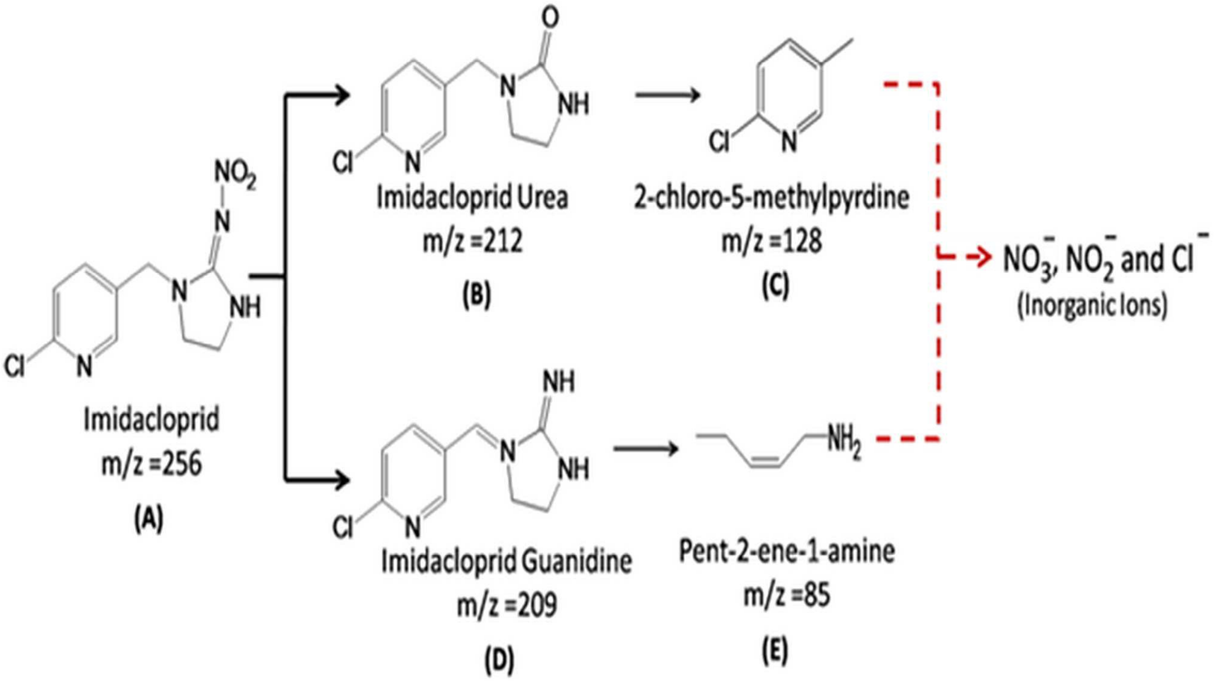
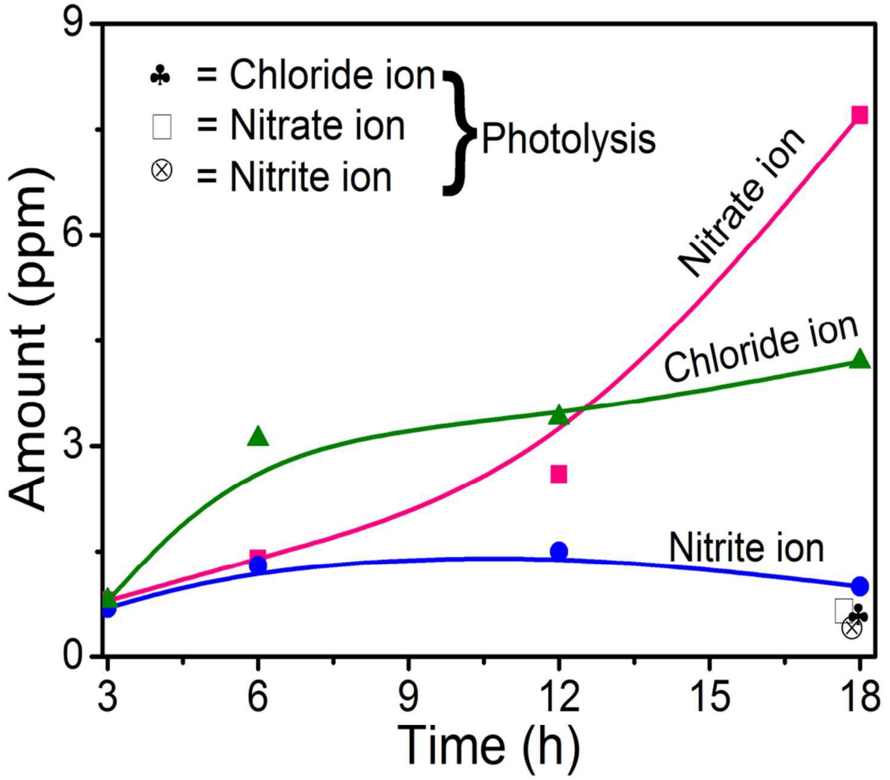


Figure 7



♣ = Chloride ion
□ = Nitrate ion
⊗ = Nitrite ion
Photolysis
Nitrate ion
Chloride ion
Nitrite ion
Amount (ppm)
0
3
6
9
Time (h)
3
6
9
12
15
18

Figure 8