

# Effect of Fe<sup>2+</sup> amendment on photodegradation kinetics of imidacloprid in moist soil

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**Abstract** The present study deals with the effect of Fe<sup>2+</sup> on degradation kinetics of imidacloprid in moist soil under UV system. The moist soil samples were spiked with imidacloprid and irradiated in specially designed UV-photoreactor. The analysis of imidacloprid was carried out by using HPLC–DAD system. UV irradiation caused about ten fold increase in photodegradation rate of the pesticide. Amendment of soil with Fe<sup>2+</sup> at concentrations of 30 mg/kg led to a further increase in the rate of photodegradation, i.e., a 98 % degradation of imidacloprid was observed in the presence of iron after 32 days of irradiation. Moreover, the half-life of imidacloprid in Fe<sup>2+</sup>-amended soil was observed to be reduced to 7 days that in the absence of Fe<sup>2+</sup> was recorded to be 21 days. Iron was also observed to affect the half-life of imidacloprid in dark. When compared with unsterilized Fe<sup>2+</sup>-amended batch treatments, the  $t_{1/2}$  in sterilized Fe<sup>2+</sup>-amended batch treatments increased from 58 to 96 days. Imidacloprid-urea was detected by HPLC as the only stable photodegradation byproduct of imidacloprid in the soil.

**Keywords** Photodegradation · Imidacloprid · Iron · Soil · UV-photoreactor

## Introduction

Imidacloprid is a systemic insecticide that is highly effective against various pests, soil insects and termites, etc (Tomlin 2000). It targets the pest by acting as an agonist of nicotinyl acetylcholine receptor. Due to its persistence in the soils, it may cause hazardous effects not only on plants and soil flora and fauna but also on human beings. Thus, it is quite imperative to study its transport, abiotic transformation and ultimate fate (Krohn and Hellpointner 2002). Various physicochemical processes are operative in soil solution that decides the environmental behavior of imidacloprid. Among these, sorption is of prime importance, as it not only affects the transport and transformation of pesticide, but also its bioavailability (Liu et al. 2002). The extent of sorption is determined by various soil properties such as organic matter content, type and content of clay, pH, cation-exchange capacity (CEC) and the physicochemical properties of the pesticide itself (Cox et al. 1998; Cupples et al. 2000).

The photodegradation of pesticides in aqueous media have been extensively studied with the focus being on the evaluation of kinetics of photodegradation (Lanyi and Dinya 2003; Zheng and Ye 2001; Gupta 2008; Liu et al. 2006). For imidacloprid, degradations of as high as 90 % were reported on irradiating its aqueous solution with 290 nm light for 4 h. The main degradation products identified were 6-chloronicotinaldehyde, *N*-methylnicotinamide, 1-(6-chloronicotinyl) imidazolidone and 6-chloro-3-pyridylmethylethylendiamine (Moza et al. 1998). The sunlight-induced photolysis of aqueous solution of

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imidacloprid was also studied on the surface of tomato leaves (Scholz and Reinhard 1999). UV-induced photodegradation (240–260 nm) of imidacloprid was studied in 10 % acetonitrile/water mixture. The mechanism of photodegradation was reported to involve N–NO<sub>2</sub> bond cleavage, hydroxylation of the imidazolidine ring and oxidative cleavage of the methylene bridge (Wamhoff and Schneider 1999).

The information on photodegradation of pesticides in soil is scarce because the interaction between soil components (i.e., organic matter and mineral oxides) and pesticides render the process of photodegradation to be complex as well as slow. However, the rates of photodegradation may be enhanced by the presence of certain metals in the soil that have the ability to alter the enzymatic activity of soil microorganism (Helal et al. 2006; Kamiya and Kamayama 2001; Kools et al. 2005; Saron et al. 2006; Shen et al. 2005). The mechanism of this catalytic enhancement is believed to involve the intermolecular attack of OH of metal hydroxides on the pesticide moieties that are ultimately degraded (Ou et al. 2007, 2008; Tajeddine et al. 2010; Wyer 2008). The main objective of the present study was to examine the effect of Fe present in the soil on the photodegradation of imidacloprid in agricultural soils. The study is important because coexistent Fe on catalyzing the photodegradation of imidacloprid may help in avoiding the hazards that may be anticipated due to accumulation of imidacloprid in agricultural soils due to its persistent nature and excessive and repeated use.

## Materials and methods

Imidacloprid standard (98 % purity), 6-chloronicotinic acid (Fluka), acetonitrile, ethyl acetate (HPLC grade) was purchased from Sigma Aldrich company Ltd. Stock solutions of imidacloprid and 6-chloronicotinic acid was prepared in methanol and stored in a freezer (<–20 °C). HPLC grade acetonitrile and water were passed through a 0.45- $\mu$ m filter prior to use. Analytical grade NaOH, Na<sub>2</sub>SO<sub>4</sub>, FeS·O<sub>4</sub>·7H<sub>2</sub>O were purchased from Merck, Germany. Sodium sulfate was baked at 500 °C for 4 h and then stored in an airtight glass bottle until use. All other chemicals used in the present experiments were of analytical grade and were used without any further purification. Deionized water was used for the processing and preparation of solutions.

## Soil collection and characterization

Soil (0–20 cm top soil) used in the study was collected from botanical garden of Lahore College for Women University, Lahore, Pakistan. Prior to use, the soil was passed through 2-mm sieve, and maintained at a 75 % water holding capacity (WHC) in accordance with the method described elsewhere (Frank et al. 2002) then stored in the dark at 20 °C until analysis. Soil texture was determined by using the hydrometer (Bao 2000). The properties of this soil are presented in Table 1. Soil samples were sterilized by autoclaving them for 2 h in a capped 100-mL Erlenmeyer flask at 121 °C.

## Photochemical experimental setup

Irradiation of the soil samples was performed in a self-designed photoreactor, equipped with a 6-W UV tube (Atlas, Linsengericht, Germany), surrounded with a thermophore jacket and water bath that circulated water through the floor of the photolysis chamber beneath the samples for temperature control. An air inlet allowed constant purging of the sample headspace. The spiked soil samples contained in Pyrex petri plates were continuously irradiated with the UV tube placed 23 cm above. A reference plate containing un-spiked soil sample was also irradiated for same time interval. Soil moisture values were recorded after every 24 h. If necessary at each sampling, the weight of each soil tray was manually adjusted with distilled water to ensure that the soil was being maintained at its initial weight and moisture content.

## Sterilized and unsterilized soil dark control test samples

In the laboratory, sandy soil samples were subdivided into two groups to investigate the dissipation rates under sterilized and unsterilized dark conditions. Each portion (10 g, dry weight) of the sample used for sterilization was autoclaved three times (at 24 h apart) for 30 min each in a capped 100-mL Erlenmeyer flask at 121 °C. Axenic water and deionized water were added to the germ-free (autoclaved) and the original (un-autoclaved) soils, respectively, to obtain a water content of 75 % by WHC. These moistened subsamples were spiked and then incubated at 25 °C in the dark 0, 24, 48, 96, 144, 192, 384 and 840 h, respectively.

**Table 1** Properties of the soil used in experiment

Soil type	% Clay	% Sand	% Silt	M.C %	O.M %	pH (1:2)	CEC (mmol/kg)	Fe (mg/kg)
Sandy	4.5	87	8.5	2.34	4.62	7.4	8.3	56

### Spiking procedure

The spiking solutions of imidacloprid were prepared by appropriate dilution of stock solution (5,000 µg/mL) with acetonitrile to a final concentration of 500 µg/mL. Soil slurries were prepared by mixing 10.0 g of soil (dry weight) with 7.5 mL water in petri plates. The soil was evenly spread across the plate to a depth of 2 mm and then spiked it with appropriate concentration of imidacloprid. Subsequently, these soil samples were spiked with Fe<sup>2+</sup> while maintaining its final concentration at 66.0 mg/kg. The spiking solution was dispensed evenly across the soil surface via micro-syringe. The soils were then mixed thoroughly and distributed uniformly in the petri plate. These sample plates were placed inside the photoreactor and irradiated for 0, 4, 24, 48, 96, 144, 192, 384 and 840 h, respectively. The control experiments with no addition of Fe were carried out simultaneously. After irradiation, the triplicate samples and control were removed from photoreactor to proceed further.

### Extraction and analysis

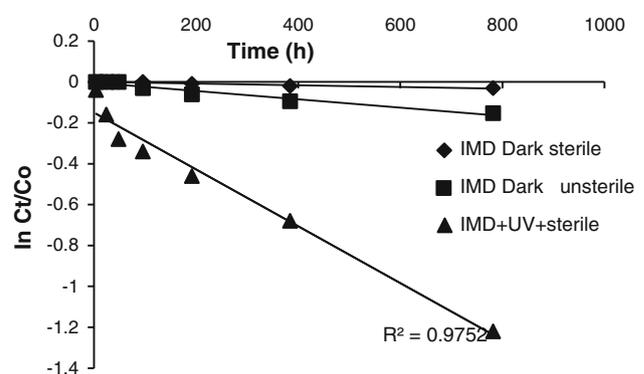
The irradiated soil samples were extracted by using the method of Graebing et al. (2004) with slight modifications (Graebing et al. 2004). Briefly, the irradiated samples were transferred to 50-mL flasks and extracted thrice with 10-mL portions of acetonitrile/water mixture containing 1 N phosphoric acid (9:1) v/v. The extraction was carried out by thoroughly vortexing and sonicating the samples for 10 min in an ultrasonic bath, and subsequently centrifuging for 10 min. The residual cake was extracted twice. The soil extracts were combined and concentrated by using vacuum evaporator set at 40 °C. The extracts were then filtered through 0.45 µm polyethersulfone (PES) syringe filter membrane (Membrane Corporation, Germany) and dried with anhydrous sodium sulfate. Subsequently, the samples were evaporated to 5 mL by using a rotary evaporator and concentrated under a gentle stream of nitrogen at ambient temperature to a final volume of 1 mL. The concentrated extracts were stored at 4 °C in glass vials for later analysis by HPLC. The extraction efficiency was found to be 88–97 % with standard deviation of ±3.5 for soil samples. An Agilent model 1,100 HPLC system equipped with DAD detector and an autosampler (model G1313A) was used for the analyses. The chromatographic column was 250 × 4.6 mm (i.d.) RP-C18 column. A multi-wavelength UV detector (model 1315B) operating at 270 nm was used. The mobile phase (1 mL min<sup>-1</sup>) used was acetonitrile–water (50:50, v/v) buffered with phosphate at pH 4.0. The retention times of 6-chloronicotinic acid and imidacloprid under the above conditions were 3.1 and 3.7 min. Calibration was performed each time samples were analyzed using external standards and the linear regression analysis were used for quantification.

In order to determine the degradation kinetics, ln (C<sub>t</sub>/C<sub>0</sub>) was plotted versus irradiation time. The degradation rate constant *k* was calculated from the slop of first-order equation: lnC<sub>t</sub> = -*kt* + lnC<sub>0</sub>, where C<sub>t</sub> represented the concentration of the pesticide at time *t*, C<sub>0</sub> represented the initial concentration, and *k* was the degradation rate constant. When the concentration was reduced to 50 % of initial pesticide concentration, the half-life (*t*<sub>1/2</sub>) was determined by the relation *t*<sub>1/2</sub> = 0.693/*k*. The tests were carried out in triplicate and the data expressed average effect of the test points (Müller et al. 2007).

## Results and discussion

### Photodegradation of imidacloprid

The photodegradation data for imidacloprid obtained after irradiation of sandy soil samples under UV verses irradiation time are depicted in Fig. 1 as natural logarithmic declines. The data for control samples are also elaborated in the figure for comparison. The data revealed that irradiation of moist soils followed first-order reaction kinetics as evidenced by linear regression lines with an *r*<sup>2</sup> value of 0.975 in accordance with previous literature for photodegradation kinetics (Graebing et al. 2004). Under the prevailing conditions, the half-life (*t*<sub>0.5</sub>) of imidacloprid photo-degraded was found to be 21 days (reaction rate of 1.4 × 10<sup>3</sup>) which was small as compared with earlier reported half-life of imidacloprid in air-dried soil that was recorded to be 39 days (US Environmental Protection Agency 1994). It was attributed to the fact that in case of air-dried soils, light was unable to penetrate deep into the underneath soil and thus there were no chances of interaction of light with the pesticide. Previously it has been described that in air-dried soils, the depth of penetration of UV light was only ~0.5 mm (Giant et al. 2005). Beyond this depth imidacloprid was unaffected by direct UV irradiation, and hence the recovered amount achieved a constant



**Fig. 1** Kinetics of degradation of imidacloprid under UV light in comparison with control

level. In case of moist soils, imidacloprid was able to move into the photolytic zone of soil through evaporation–condensation cycles where it was degraded efficiently on irradiation. Furthermore, indirect photolysis by hydroxyl radical, singlet oxygen, and other radical species were believed to enhance the rate of photodegradation (Graebing et al. 2004).

Imidacloprid did not degrade in the dark in both sterile and unsterile ( $p$ ) 0.75 for unsterile moist soil, ( $p$ ) 0.25 for sterile moist soil. The difference in the overall reaction rates between the dark control experiments was not significant ( $p > 0.05$ ). This demonstrated that the key process for imidacloprid degradation under natural conditions was photodegradation. The rate constant for the degradation of imidacloprid in the dark was  $2.0 \times 10^{-4}$  with a half-life of 144 days (Fig. 1). The rates of degradation as evaluated based on first-order kinetics for imidacloprid in dark and in presence of UV-C light are presented in Table 2. The rate of imidacloprid photodegradation was observed to increase in UV system from  $2.0 \times 10^{-4}$  to  $1.4 \times 10^{-3}$  with half-life of 21 days only.

During the present study, imidacloprid-urea was produced as the stable degradation product of imidacloprid and its formation was found to be linearly associated with degradation of imidacloprid (Fig. 2). Up to the period of 120 h of UV irradiation, its concentration was found to be directly correlated with imidacloprid decay in soil (Fig. 2), i.e., imidacloprid-urea concentration increased and imidacloprid concentration decreased on UV irradiation. However, after 5 days its concentration was recorded to be decreased with a decrease in concentration of imidacloprid in the soil. This fact indicated that photodegradation of imidacloprid-urea was also initiated after 5 days that evidenced the onset of mineralization of imidacloprid.

#### Effect of initial concentration of pesticide

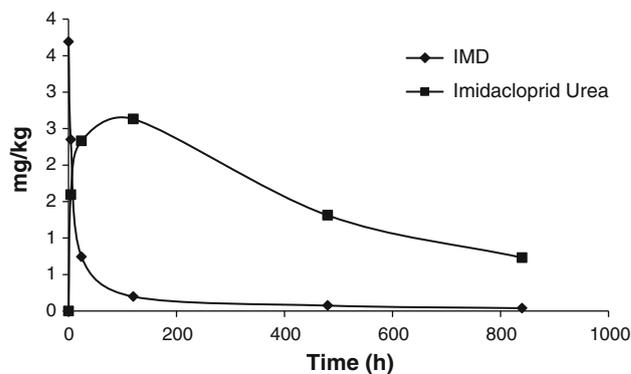
Photodegradation rate of imidacloprid was observed to decrease by increasing its concentration in soil as depicted in Fig. 3. When the initial concentration of imidacloprid in soil was raised from 10 to 50 mg/kg, the rate of reaction was observed to be increased. The data thus evidenced the

inverse dependence of rate constant on initial concentration of imidacloprid that may be explained based on increased competition between imidacloprid and its photodegradation products for limited number of photons present in irradiated light (Valeria et al. 2010).

#### Effect of iron amendment on imidacloprid degradation

Iron has been known to accelerate the photolysis of organic compounds in soil through photosensitizing effect (Giant et al. 2005; Salah et al. 2006). Irradiation of imidacloprid in moist soils in presence of iron followed first-order reaction curve as evidenced by an  $r^2$  value of 0.9776 (Fig. 4). The rate of photodegradation was observed to be  $4.1 \times 10^{-3} \text{ h}^{-1}$  with a half-life of 169 h.

A threefold increase in percent degradation of imidacloprid with significant decrease in the half-life ( $t_{0.5}$ ) was observed due to catalytic addition of iron, i.e., the half-life decreased from 21 to 7 days. The results of present study were well in agreement with the results of previous studies where catalytic activities of iron in different forms were used for the removal of imidacloprid from aqueous systems (Comfort et al. 2001; Eggen and Majcherczyk 2006; Menager 2007; Mestankova 2004; Valeria et al. 2010; Yang et al. 2010), but to date no such study is available that

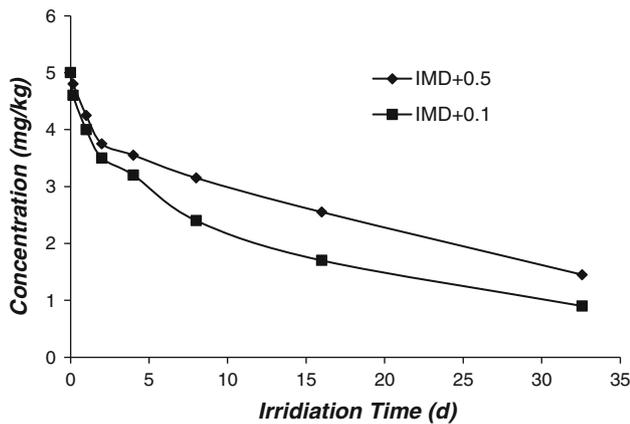


**Fig. 2** Kinetics of degradation of imidacloprid and 6-chloronicotinic acid

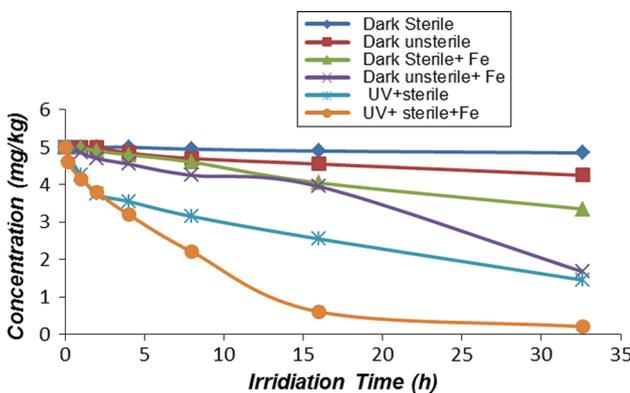
**Table 2** Degradation characteristics of imidacloprid in soil amended with  $\text{Fe}^{2+}$

	Environment	$\text{Fe}^{2+}$ level in soil <sup>b</sup>	Degradation equation $\ln C^t = -\ln C^0 - kt$	Correlation coefficient $r^2$	$t_{1/2}$ (days)
Imidacloprid 50 mg/kg	UV	$C_{\text{Fe}}^{\text{a}}$	$-0.1503 - 0.0014t$	0.9752	21
	UV	$C_{\text{Fe}}^{\text{o}} + 10$	$-0.1076 - 0.0041t$	0.9776	7
	Dark sterile	$C_{\text{Fe}}^{\text{o}}$	$-0.0038 - 0.0002t$	0.9563	144
	Dark sterile	$C_{\text{Fe}}^{\text{o}} + 10$	$-0.0151 - 0.0003t$	0.9536	96
	Dark unsterile	$C_{\text{Fe}}^{\text{o}}$	$-0.0038 - 0.0006t$	0.9563	144
	Dark unsterile	$C_{\text{Fe}}^{\text{o}} + 10$	$0.0088 - 0.0005t$	0.9979	58

<sup>a</sup>  $C_{\text{Fe}} = 56 \text{ mg/kg } \text{Fe}^{2+}$  as a control treatment without the addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to soil



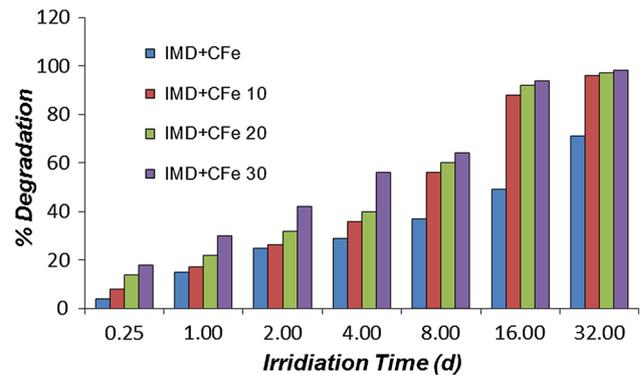
**Fig. 3** Effect of concentration of imidacloprid on its photo-degradation



**Fig. 4** Degradation pattern of imidacloprid in different environments

focuses on the remediation of imidacloprid in soil. The present study is first effort to this effect.

The dissipation rates of imidacloprid increased slightly in iron-amended soil in dark during 32 days of incubation when compared with the control treatments; the imidacloprid degraded in unsterile iron amended with  $t_{1/2}$  of 58 days as compared to sterile iron-amended soil ( $t_{1/2} = 96$  days) (Fig. 4). These results were supported by the fact that heavy metals influence the dissipation of pesticides by affecting the activity of soil microorganisms. However, this degradation in the dark in the presence of Fe was found to be slow in comparison with its degradation in UV system. In fact, the half-life of imidacloprid degradation was observed to be decreased from 58 to 7 days, when imidacloprid amended with catalytic amount of iron was exposed to UV light, which indicated enhanced efficiency of imidacloprid degradation. Liu et al. (2006) have reported that the hydrolysis of imidacloprid in neutral solution was also slightly catalyzed by the presence of  $Fe^{3+}$  in clays. Under these considerations, a degradation of only 1.7 % of imidacloprid was observed in the presence of  $Fe^{3+}$  bound



**Fig. 5** Effect of  $Fe^{2+}$  concentration on photodegradation of imidacloprid

to bentonite, after 90 days of incubation (Liu et al. 2006). However, the present study affords degradation of imidacloprid in presence of  $Fe^{2+}$ -UV system to be 88 % after 16 days of irradiation.

#### Effect of iron concentration on degradation

Photodegradation of imidacloprid was found to be enhanced in presence of  $Fe^{2+}$  in UV system. After an exposure of 24 h of UV light, imidacloprid was observed to be degraded to only 15 % of its original concentration. Its rate of degradation was increased up to ~30 % when iron was amended at a concentration of 30 mg/kg. The percent photodegradation of imidacloprid was found to be to 56, 60, and 64 % in presence of iron concentrations of 10, 20, and 30 mg/kg, respectively, with a constant UV light exposure of 192 h (Fig. 5).

#### Conclusion

On the basis of above results of the study, it was concluded that photodegradation is the major decomposition pathway for imidacloprid in soil and the presence of iron in the soil may significantly enhance this rate. In fact, the half-life of imidacloprid was decreased from the reported 39 to 7 days in UV +  $Fe^{2+}$  system. In the absence of UV light (i.e., dark) as well,  $Fe^{2+}$  catalyzed the degradation of imidacloprid slightly. The concentration of  $Fe^{2+}$  also had profound influence on the rate of photodegradation. In view of these considerations, trace amounts of Fe, if present in agricultural soil, may help in getting rid of very persistent imidacloprid, and avoid hazards that may arise due to its long-term use.

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