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Photodegradation of α-cypermethrin in soil in the presence of trace metals (Cu^{2+}, Cd^{2+}, Fe^{2+} and Zn^{2+})

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Abstract

The influences of trace metals (Cu^{2+}, Zn^{2+}, Cd^{2+} and Fe^{2+}) on the photodegradation of α-cypermethrin (α-CYM) in agricultural soil were studied. The soil samples were spiked with α-cypermethrin with/without the presence of metal ions, irradiated under UV irradiation chamber for a regular period of time and analyzed by using HPLC. The dark control sterile and unsterile soil samples spiked with α-cypermethrin and selected trace metals were incubated for the same interval of time at 25^{o}C. The results obtained indicated that photodegradation of α-cypermethrin followed first-order and biphasic kinetics. The photodegradation half-lives (t½) of α-cypermethrin were found to be increased from 2.3 hours to 7.9, 5.4 and 3.2 hours in the presence of Cu^{2+} Zn^{2+} and Cd^{2+} respectively. Fe^{2+} increased the photodegradation kinetics from -0.299 h^{1-} to -1.849 h^{1-} and varied the t$_{1/2}$ from 2.32 to 0.37 h^{1-} in the soil. Microbes also affected the degradation of α-cypermethrin in metal contaminated soil. The degradation rate was inhibited in unsterile soil and the order of inhibition was found to be: Zn^{2+}< Cd^{2+}< Cu^{2+}. The degradation/ persistence of α-cypermethrin were affected linearly with the increasing soil metal concentrations. Cd^{2+} and Fe^{2+} accelerated the abiotic dissipation by increasing the reaction rate from -0.024 h^{1-} to -0.032 h^{1-} and -0.029 h^{1-} respectively.

Key words: photodegradation; trace metals; α-cypermethrin; agricultural soil; HPLC

1. Introduction

The use of pesticides to increase the crop production is a common practice in the world. These practices however, generate residues that may be noxious to the environment. The accumulation and degradation of these pesticides and their dispersion in the environment depends on the characteristics and overall functions of the ecosystem[1] . α-Cypermethrin (α-CYM) is widely used to control the Helicoverpa spp., the major pests of cotton. It is highly hydrophobic as reflected by its low water solubility and high octanol–water partition coefficient (Table 1). Low solubility and high lipoaffinity make it a highly toxic agent to fish and aquatic invertebrates even at very low levels (<0.5 µg L1^{-}, LD$_{50}$ values)[2]. Moreover, it is metabolized and eliminated significantly more slowly by fish than by mammals or birds that explains its higher toxicity to fish than other organisms[3]. Generally, the lethality of pyrethroids to fish increases with the increasing octanol/water partition coefficients[4]. US Environmental protection agency (EPA) has also classified it as a possible human carcinogen.

A large proportion of cotton grown is irrigated by drainage water, thus the risk of environmental damage may also be significant[5, 6]. Moreover, pesticides when applied to soil as insecticides are not selective and may also kill beneficial soil microorganisms[7, 8]. α-Cypermethrin is moderately persistent in the soil environment with field half-lives ranging from 4 to 12 weeks[9, 10]. Due to its high hydrophobic property, it causes strong sorption to soil particles, which may cause buildup of bound residues[11- 13].

Organic wastes and sludge are commonly applied to the agricultural soils as a source of organic material and to improve the soil properties[14]. However, some studies have shown that the addition of organic manure, and N and P fertilizers can affect the pesticide degradation in the soils[15-18]. Moreover, the use of these materials can lead to the problems associated with their heavy metal contents, especially their successive applications may result in heavy metal accumulation in the soil.

Pyrethroid can undergo photolysis in the soil with half-lives ranging from 5 to 170 days[9]. Enhanced concentrations of heavy metals and their strong binding with soil organic matter and clay minerals may lead to their persistence in the soil. This results in a slow dispersion of synthetic pyrethroids and their potential for long-term effects on beneficial soil microorganisms and aquatic species[1, 19]. Liu et al. (2007) have reported that the presence of Cu^{2+} (10 mg kg^{1-}) in the soil may inhibit the degradation of cypermethrin (increases $t_{1/2}$ from 8.1 to 10.9 d) that may be explained as the reduction in activity of bacterial biomass due to Cu^{2+}[20]. Some of the metals like iron are known to enhance the degradation of pesticides and reduce their half-lives[21, 22].The dissipation/persistence of pesticides in presence of trace metals was due to their effect on growth rate of the pesticide degrading bacterial populations [23, 24]. For example, the carbendazim degrading Variovorax and the diuron degrading Rhodococcus strains were extremely sensitive to Cd^{2+} as it decreased their degrading activity even at low concentrations. Cu^{2+} ions strongly inhibited the degradation process of ethylenethiourea (ETU) which is an important degradation product of ethylenebisdithiocarbamate fungicides while 2,4D-degradation by Variovorax was highly accelerated by Cu^{2+} ions. Zn^{2+}, Cu^{2+} and Mn^{2+} (20-50 mg L^{1-}) accelerated the carbendazim and diuron degradation[23, 24]. Therefore the goal of the present study was to determine the influence of Cu^{2+}, Cd^{2+}, $Fe^{2+}$and Zn^{2+} ions on the dissipation/persistence of α-cypermethrin in the soil. The study is important because the trace metal levels in agricultural soil can enhance the catalytic photodegradation of pesticides. So major hazards related to excessive and repeated use of pesticides in the agricultural soils may be abated in this way.

2. Materials and Methods

2.1 Test Materials and Reference Standards

Reference standard of α-cypermethrin (99% purity) was obtained from Sigma-Aldrich, Ltd. (USA). The physical properties of α-cypermethrin as provided by "OECD[25] guidelines for the photodegradation of pesticides on soil surface"are listed in Table 1. HPLC grade methanol, acetonitrile, ferrous sulphate, zinc chloride, cadmium chloride, copper sulphate ($CuSO_4•5H_2O$) and anhydrous Na_2SO_4 (analytical Grade) were purchased from Merck (Darmstadt, Germany). Highly pure double distilled water for use during experiment was prepared with a Milli-Q system from Millipore-Waters Co. (Bedford, MA). Na_2SO_4 was baked at 500°C for 4 h before the beginning of experiment and then stored in an airtight glass bottle until use.

2.2 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. 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[26]. It was then stored in the dark at 20°C until analysis. Soil texture was determined by using the hydrometer[27]. The physical and chemical properties of the soil sample were measured by using the methods of Saltanpour and Schwap (1977)[28] and summarized in Table 2. Soil was cleaned from pesticides by stirring it with acetone for 24 h (three times) and after decanting the acetone, it was dried first at room temperature and then in oven at 105 °C. Soil sample were sterilized by autoclaving for 2 h in a capped 100-mL Erlenmeyer flask at 121°C[29].

2.3 Photochemical experimental set up

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 thermopore jacket and water bath that circulated water through the floor of the photolysis chamber for temperature control. An electric fan (3 volt) fitted inside the radiation chamber 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 unspiked soil sample was also irradiated for the same time interval. Soil moisture values were recorded first after every hour and subsequently after every 6 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.

2.4 Control sterilized and unsterilized soil dark samples

In the laboratory, control soil samples were subdivided into two groups to investigate the dissipation rates under sterilized and unsterilized dark conditions. The unsterilized samples were used as bioactive controls and were not given any acetone wash. 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. Double de-ionized water was added to the germ-free (autoclaved) and original (un-autoclaved) soils to obtain the water content of 75% by WHC. These moistened sub-samples were spiked with pesticide and then incubated at 25°C in the dark for 0, 24, 48, 96, 144,192, 384 and 762 h respectively.

2.5 Standard solution preparations and spiking procedure

The spiking solutions (0.5µg g^{1-}) of α-cypermethrin were prepared by appropriate dilution of stock solution (5µg g^{1-}) with acetonitrile. For metal assisted degradation tests, stock solutions of $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $CdCl_2$ and $ZnCl_2$ were prepared at concentrations of 1000 mg L^{1-} in water. These stock solutions were then diluted to 100 mg/L for use as a source of external Cu^{2+}, Fe^{2+}, Cd^{2+} and Zn^{2+} ions. Soil samples were spiked with α-cypermethrin at the maximum field concentration of 0.5 mg kg^{1-}. The final concentrations of Cu^{2+} in the soil were set at 15.9 (control treatment), 25.9, 35.9 and 45.9 mg kg^{1-}, for Zn^{2+} final concentrations were 26.9 (control treatment), 36.9, 46.9 and 56.9 mg kg^{1-}, for Cd^{2+} 0.7 (control treatment), 10.7, 17.7 and 27.7 mg $kg^{1-}$and for Fe^{2+} these final concentrations were 863 (control), 873, 883 and 893 mg kg^{1-} (triplicate samples) of each concentration were measured. After soil treatments, the samples were incubated at 25°C in the dark at a moisture content of 75%. The residual contents in the sterilized and unsterilized samples were monitored at regular intervals as described above.

Soil slurries were prepared by mixing 10.0 g of soil (dry weight) with 7.5 mL of water in petri plates. The soil was evenly spread across the plate to a depth of 2 mm and then spiked with appropriate concentration of pesticide. Subsequently, these soil samples were spiked separately with Cu^{2+}, Cd^{2+}, Fe^{2+} and Zn^{2+}. To this effect, different volumes of diluted metal solutions were dispensed evenly across the soil surface via micro-syringe while maintaining the similar moisture level for all the samples. Soil samples were manually shaken to homogenize them. The petri plates were then placed inside the photoreactor and irradiated for 0, 4, 24, 48, 96, 144,192, 384 and 762 h respectively. Control experiments with no addition of trace metals were carried out simultaneously. After irradiation, the triplicate samples and control were removed from the photoreactor and processed further.

2.6 Pesticide Extraction and analysis

USE method which is an extension of EPA method 3550C was used for extraction of α-cypermethrin from the soil[30]. Briefly, the irradiated soil samples were placed in 50 mL Erlenmeyer flasks and extracted with 10 mL of ethyl acetate. These samples were first manually agitated and then exposed thrice to USE in a 100H (80/160 W) ultrasonic bath (Sonorex, Germany) for 15 min. After each extraction, extracts were collected by pouring the extractant through a funnel plugged with a small piece of cotton wool overlaid by a portion of anhydrous sodium sulfate which had been previously washed with the same solvent. In order to achieve the adequate concentration factor, 10 g aliquot of the sample was submitted for extraction and the final extract (ca. 30 mL) was evaporated to dryness using rotary evaporator and gentle steam of nitrogen without need of any clean-up procedure and reconstituted in 1 mL acetonitrile. The extraction method showed good efficiency and reproducibility with mean recoveries of 73–92% with standard deviations lower than 2.4% for the whole procedure.

α-Cypermethrin was analyzed by using the method of Metwally et al., 1997[31] and Martnez et al.**.** 1996[32]. HPLC system consisting of Agilent model 1100 pump, equipped with DAD detector, an autosampler (model G1313A) and C8 chromatographic column (Bondsil, 15x0.46 cm, 5 urn particle size, Analytichem International) was used for analysis. Mobile phase (acetonitrile/water 75/25) at flow rate of 1 mL/ min was used. The areas of eluted peaks detected at 225 nm were recorded by using a multi- wavelength UV detector Model G 1315B. The retention time of α-cypermethrin under the above conditions was 8.3 min. Calibration was performed each time when samples were analyzed by using external standards. HPLC procedure was linear in the range 0.01-100 µg mL^{1-} at 225 nm with regression coefficient of 0.994 (± 0.02) ($n = 12$); the detection limit was 0.02 µg mL^{1-} and limit of quantification was 0.18 µg mL^{1-} .

2.7 Data analysis

In the soil, the photolytic decline of a pesticide slows down with time, either due to the adsorption of pesticide to soil or its movement out of a photic zone. Thus the Langmuir–Hinshelwood (L–H) kinetics has been suggested for the photodegradation of pesticides. This model is based on the following equation:

$$r = dC/dt = (kKC/2) + KC$$

Here r represents the rate of mineralization of pesticide, C = pesticide concentration, k = rate constant, and K = pesticides adsorption coefficient. Under the conditions of smaller initial concentration (C_0) i.e. in ppm range, many researchers have approximated this L–H kinetics to first-order expression just to obtain the parameters involved in the L–H equation easily[33].

However, when lag phase was involved, the Hockey-stick model was used for the evaluation of kinetics. This model is based on two sequential first-order curves. The pesticide concentration initially declines according to first-order kinetics with a rate constant k_1. At a certain point in time (referred to as the breakpoint), the rate constant changes to a different value k_2. Mathematically, this model is described as:

$$dM/dt = -k_1M \quad \text{for } t \leq t_b$$

$$dM/dt = -k_2M \quad \text{for } t > t_b$$

where

M = Total amount of pesticide present at time t

M_0 = Total amount of pesticide applied at time t=0

k_1 = Rate constant until $t=t_b$

k_2 = Rate constant from $t=t_b$

tb = Breakpoint (time at which rate constant changes)

$$DT_x = \frac{\ln 100/100\text{-}x}{k_1} \qquad \text{if} \quad t \leq t_b$$

$$DT_x = t_b + \frac{[\ln 100/100\text{-}x - t_1 b]}{k_2} \qquad \text{if} \quad t \leq t_b$$

The tests were carried out in triplicate and the data was expressed as average effect of the test points[34].

3. Results and discussion

α-cypermethrin was chemically stable in neutral soil condition with half-life of 101 days. It was microbically degraded with $t_{1/2}$ of 13 weeks, but its photodegradation was only reported on soil surface as thin film (Table 1). No soil incorporated photodegradation study has been reported up till now.

3.1 Photodegradation of soil incorporated α-cypermethrin

The presence of unstable groups such as isobutyl and double bonds in the structure of pyrethroids renders them to degrade usually through photolysis, photooxidation and photoisomerization in the natural environment[35]. The photodegradation data of α-cypermethrin obtained after irradiation of soil samples under UV system versus irradiation time is depicted in Fig.1. The data for control samples is also elaborated in the same figure for comparison. The photodegradation and photocatalysis rates of pesticides on soil surfaces under UV light depend on different parameters such as temperature, soil particle sizes, soil depth responsible for photodegradation and catalyst loads[36].

The present study revealed that soil incorporated α-cypermethrin photodegraded quickly under UV photoreactor with the half-life of approximately 2.3 ± 1.41 days (Table 3). Previous studies have reported the half-lives of 8-16 days for the photodegradation of cypermethrin on soil surfaces[37]. In sandy soils, its half life was reported to be 2-4 weeks[38]. It has been found that cypermethrin degrades more rapidly on sandy loam and sandy clay soils than on clay soils and more rapidly in soils with low organic matter [39, 40]. Raikwar and Nag, (2011) reported the half-life of α-cypermethrin under UV system to be 0.93 h in clay loam and 1.57 h on loam soil[41]. In fact only 8% of radiant solar energy is comprised of UV spectrum and on reaching the earth's surface, its intensity is further decreased. In case of laboratory experiments, the source emits 100% only UV radiations with most of the intensity directed on the samples that is why lower half lives were observed in the present study and in all other studies carried out under laboratory UV irradiated systems as compared to the studies carried out on sunlit soil surfaces.

Pesticides photodegradation was slow in dry soil as light was unable to penetrate deep into the underneath soil and there were no chances of interaction of light with the pesticide, thus moist soil was used in the present study in accordance with the findings of Graebing et al., (2004)[42]. α-Cypermethrin is likely to volatilize as indicated by its low Henrys Law constant therefore it can move into the photolytic zone of soil through evapo-condensation cycles where it degrades efficiently on irradiation. Furthermore, indirect photolysis by hydroxyl radicals, singlet oxygen and other radical species were believed to enhance the rate of photodegradation in moist condition[42].

3.2 Microbial degradation of α-cypermethrin

Microbes also play significant roles in degrading and detoxifying the α-cypermethrin residues in the environment[11, 43]. The large difference between reaction rate (-0.044) and $t_{1/2}$ (18.18 hours) at $p < 0.05$of unsterilized and sterilized soils indicated the role of biotic degradation (Fig. 1 and Table.3).When compared with the photodegradation, the $t_{1/2}$ of the unsterilized treatments was increased by 5 fold. Tallur et al., (2007), studied that *Micrococcus sp*. present in the soil utilized cypermethrin as a sole source of carbon leading to hydrolysis of ester linkage to yield 3- phenoxy benzoate [44]. Sterilization eliminates the microbial population of the soil and thus increases the persistence of the pesticide. α-Cypermethrin dissipation in the sterile soil in dark may be attributed to the chemical dissipation because the possibility of photodegradation was ruled out by incubating the samples in the dark [45]. In the soil, the chemical dissipation of cypermethrin takes place through hydrolysis whereby the ester linkage is first hydrolysed leading to the formation of 3-phenoxybenzoic acid (PBA) and cyclopropanecarboxylic acid derivatives[46], principally, 3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropanecarboxylic acid (DCVA)[43]. Although, it is biodegradable pesticide but the microbial release of bound residues occurs rather slowly[47].

3.3 Effect of trace metals on photodegradation

The photodegradation rates of some pesticides may be enhanced in the presence of certain metals in the soil by altering the enzymatic activity of soil microorganisms[22, 48-51]. Similarly, trace metals are also known to inhibit the enzymatic reactions of microorganism by complex formation with the substrate, combination with the protein-active sites of the enzymes, or reaction with the enzyme-substrate complex. Thus bacterial biomass activity may also be inhibited in metal polluted soils. Kools et al. (2005) have reported a positive correlation between glyphosate degradation rates and soil metal pollution[49].

3.2.1 Effect of Cu^{2+}on α-cypermethrin

Photodegradation rate of α-cypermethrin was decreased from -0.299 to -0.088 when 10 mg kg^{1-} of Cu^{2+} was added to the soil as evidenced by an increase in $t_{1/2}$ from 2.32 to 7.88 ± 0.92 hours at $p < 0.05$ (Table.3). The percent photodegradation of α-cypermethrin in the presence of 25.9 mg kg^{1-} (C^o+10 mg kg^{1-}) of Cu^{2+} was decreased from 95.7 to 61.7 % after 8 days of continuous UV irradiation (Fig.3-c). This retarding effect became pronounced when Cu^{2+} concentration was increased to 45.9 mg kg^{1-} (C^o+30 mg kg^{1-}), the % photodegradation was observed to be reduced to only 50.5%. Cu^{2+} is known to enhance the photodegradation of pyrethroids in the presence of UV light[1, 52]. According to Sykora, (1997) Cu^{2+} compounds may act as catalyst for photodegradation of various pollutants in irradiated systems. The pollutants like α-cypermethrin may act as ligands in the coordination sphere of the Cu^{2+} and a Cu^{2+}-Cu^{1+} photocatalytic redox cycle was believed to occur in Cu^{2+} amended solutions. This catalytic effect might also arise due to secondary thermal reactions of the active species produced photochemically from the Cu^{2+} complex[53].The degradation rate of pesticides in the soil was closely related to its availability to the enzymatic systems of microorganisms [54, 55].

The dissipation rates of α-cypermethrin decreased significantly at $p > 0.05$ in unsterilized soil during 32 days of incubation when compared with the dark control sterile treatments (Fig. 2-a, Fig.5-a). The half-life of α-cypermethrin was observed to be increased from 10.2 ± 2.17 to 12.4 ± 2.13 hours in unsterile control treatment that indicated that Cu^{2+} affected the activity of soil microbes involved in the degradation of the pesticide (Table.3). The results of present study were compatible with the findings of Liu et al., (2007)[1] who reported that the persistence of α-cypermethrin was increased from 8.1 to 10.9 d in the presence of 10 mg kg^{1-} Cu^{2+} ion in unsterile soil. The observed degradation might be due to the fact that metals react with the sulfhydral group of enzymes thereby leading to inhibition of their activity[1]. Ellis et al., (2001) and Fernandes et al., (2005) found that Cu^{2+}-tolerant communities may have replaced the soil microorganisms that were able to co-metabolize the pyrethroids [56, 57]. Moreover, soil microbial community was adversely affected by the presence of elevated concentrations of Cu^{2+}. Cu^{2+} ions have been reported to strongly inhibit the degradation of ethylthiourea (ETU)[24]. Different initial concentrations were observed in the Fig. 3. The observation evidenced that the addition of Cu^{2+} caused the persistence of α-cypermethrin in the soil just after its addition. Fig. 4 also depicted an initially high rate of degradation that was later on reduced after some days and then stalled completely. This fact may be interpreted on the basis that desorption controls the biodegradation process[58]. The sorption of the substance determines its availability for microbial degradation. The sorbed chemicals are less accessible to microorganisms that utilize exclusively or preferentially chemicals in solution. Thus with passage of time, the sorbed quantity of pesticide is increased and their rate of degradation is reduced. It is generally accepted that sorption limits the degradation of pesticides by reducing their partitioning into the soil.

Cu^{2+} ions also affected the abiotic degradation of α -cypermethrin and thus exhibited an inhibitory effect. The inhibitory effect was more pronounce when the Cu^{2+} concentration were increased up to 45.9 mg kg^{1-}. The percent degradation of α-cypermethrin was decreased from 26.5% to 20.5% (Fig.5-c). These findings pointed toward the fact that α-cypermethrin dissipation in the soils containing low concentrations of added Cu^{2+} was more dependent on biological dissipation than chemical dissipation, but when high concentrations of added Cu^{2+} was present in soils it depended on chemical dissipation.

3.3.2 Effects of Zn^{2+}on α-cypermethrin

Zn^{2+} addition decreased the degradation of α-cypermethrin but the inhibitory effect was less severe than for Cu^{2+} (Fig. 1-c, Table 3). The photodegradation of α-cypermethrin was decreased from 95.69 to 79.5% after 8 days of continuous UV irradiation. The degree of inhibition was increased with an increase in the soil Zn^{2+} concentration from 16.9 mg kg^{1-} to 36.5 mg kg^{1-} (i.e. from C^o +10 mg kg^{1-} to C^o +30 mg kg^{1-}).

Zn^{2+} also inhibited α-cypermethrin degradation in unsterile dark incubation. The rate of reaction was observed to be increased from -0.024 to -0.040 h^{1-} resulting in an increase in t1/2 from 10.19 ± 1.92 to 21.66 ±1.10 (Table. 3). Different initial concentrations were observed in the Fig. 3, evidencing that the addition of Zn^{2+} in the soil caused the persistence of α-cypermethrin just after its addition. The % dissipation was decreased from 64.55 to 57.26 % after 32 days of continuous incubation (Fig.4-b). This might be due to a change in the functional diversity of the microbial community. Under the Zn^{2+} stress i.e., high Zn^{2+} concentrations, some soil microbial populations were shifted from sensitive to less sensitive areas, and hence soil microbial population was affected thereby leading to their weakened activities[45]. Kamitani et al. (2006) reported that there was a positive correlation between available Zn^{2+} content of soil and soil metabolic quotient, and a negative correlation between available Zn^{2+} content and microbial biomass, carbon microbial biomass, nitrogen and the microbia1 quotient[59]. No significant differences were observed in the dissipation of α-cypermethrin under the dark sterile conditions at $p > 0.05$ in the presence of soil Zn^{2+} load. It was therefore suggested that microorganisms are the major agents that are involved in the dissipation of pyrethroids in the soil environment[60].

3.2.3 Effects of Cd^{2+} on α-cypermethrin

The reaction rate of α-cypermethrin in soil was observed to be decrease from -0.299 to -0.871 at $p < 0.05$. This resulted in an increase in persistence of α-cypermethrin from 2.32 ± 1.41 to 3.20 ± 2.01 hours under UV- irradiation system. In fact, when the concentration of soil Cd^{2+} was increased from 0.7 to 30.7 mg kg^{1-} (C^o+ 10 mg kg^{1-} to C^o+ 30 mg kg^{1-}), the % degradation was decreased from 95.68 % to 65.9 % after 8 days of continuous UV irradiation. On the contrary, the successful elimination of the harmful pesticide (methomyl) was reported previously by using a Cd^{2+} based photocatalyst under the sunlight radiation within a very short time with a removal capacity being 1,000 mg pesticide per gram of the photocatalyst[61].

Cd^{2+} decreased the half-life of α-cypermethrin in dark unsterile conditions from 10.19 ± 1.92 to 7.15 ± 0.43 days (Fig.4-c). Similarly, $t_{1/2}$ in sterile conditions was decreased from 28.88 ± 1.53 to 23.90 ± 0.591 hours (Fig.5-c). Although, there are certain pesticide degrading strains of bacteria that are extremely sensitive to Cd^{2+} and Cd^{2+} decreases their degrading activity even at low concentrations[24] but in fact both the biotic and abiotic dissipation of pyrethroids occur in soil simultaneously[62]. Under sterile conditions in soils, chemical dissipation becomes more important in the presence of high concentrations of added Cd^{2+}.

3.2.4 Effects of Fe^{2+} on α-cypermethrin

Iron is one of the major elements present in the soil mostly in the forms of hydroxides/oxides/chlorides. Generally the most dominant oxidation state is $Fe^{3+}$and when reducing conditions (like subsurface environment) are prevailing, iron exists as Fe^{2+} [63]. Fe^{2+} is known to accelerate the photolysis of pesticides through photosensitizing effect [64-67]. Rafique et al., (2014) evidenced that a 3-fold increases in percent degradation of imidacloprid was observed in moist soils by the catalytic addition of Fe^{2+} to soil[22]. The present study also evidenced an accelerated photodegradation of α-cypermethrin under UV chamber by the addition of Fe^{2+}. The half-life was observed to decrease from 2.32 ± 1.41 to 0.37 ± 2.07 hours. These results are in agreement with the findings of several other authors who reported that Fe^{2+} catalyzed the photodegradation of several pesticides [22, 68, 69]. The degradation of α-cypermethrin in soil was more efficient when soil Fe^{2+} levels are enhanced. It degraded up to approximately 94 to 96% of initial concentration after 4 days of continuous UV irradiation in the presence of Fe^{2+} (C^{o} +10 mg kg^{1-} and C^{o} + 30 mg kg^{1-}) as compared with control of 74%. This enhanced effect was the result of direct Fe^{2+} catalyzed photodegradation or indirect photolysis due to the reaction of Fe^{2+} with OH^{-} radicals from moist soil. Different initial concentrations of pesticide were observed in the Fig. 3, before and after the addition of Fe^{2+} in the soil samples that evidenced the fact that the addition of Fe^{2+} in the soil caused the instant degradation of α-cypermethrin in the soil.

Soil microbes are more efficient in degrading the α-cypermethrin in the presence of higher Fe levels (C_{Fe}+30 mg kg^{1-}) as evidence by % degradation that was increased from 71.2 % to 96% in the presence of 30 mg kg^{1-} Fe^{2+}after 32 days of incubation. The zero valent iron (Fe^{0}) has already been used as remedial tool to enhance the degradation of HCHs and DDX in soil[70]. The soil Fe^{2+} levels also affected the abiotic dissipation of α-cypermethrin in soil i.e. a reduction in half life α-cypermethrin was observed from 28.88 to 21.66 days (Table.3). The % degradation was enhanced from 26.6 to 46.1% after 32 days of incubation in dark at 25 °C. Singhal et al., (2012) reported the degradation of malathion by zero-valent Fe nano-particles[71]. When it was added to the soil under anaerobic conditions, corrosion (oxidation) of the iron might be effectively coupled to reductive dechlorination and nitro group reductio[72].

Conclusions

It is concluded that photodegradation of α-cypermethrin was retarded in the presence of elevated concentrations of Cu^{2+}, Zn^{2+} and Cd^{2+}. Cu^{2+} was evidenced to possess slightly greater inhibition effect than Zn^{2+} and $Cd^{2+}$and increased the $t_{1/2}$ from 2.3 hours to 7.9 hours. Cu^{2+}, Zn^{2+} and Fe^{2+} also retarded the microbial degradation of α-cypermethrin while Cd^{2+} and Fe^{2+} accelerated the abiotic dissipation by decreasing the $t_{1/2}$ from 28.88 h to 23.90 h and 21.66 h respectively.The proliferated soil Fe levels however enhanced the photo and microbial degradation of α-cypermethrin.

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Figures

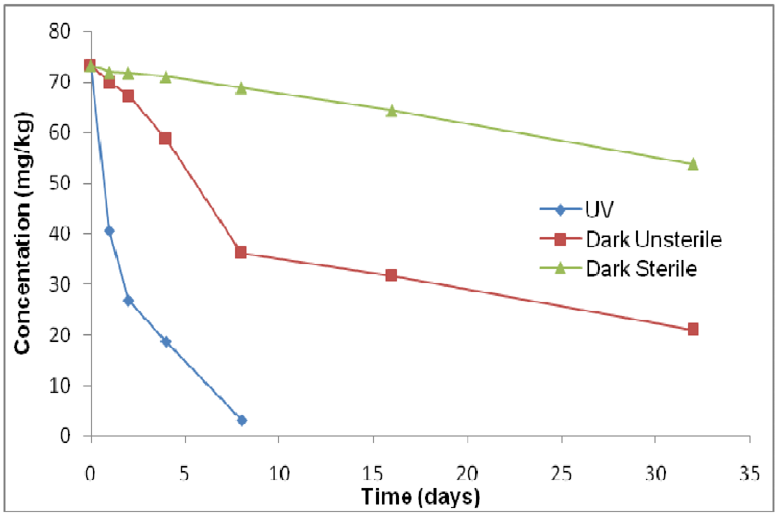

Fig.1 Photodegradation of soil incorporated α-cypermethrin

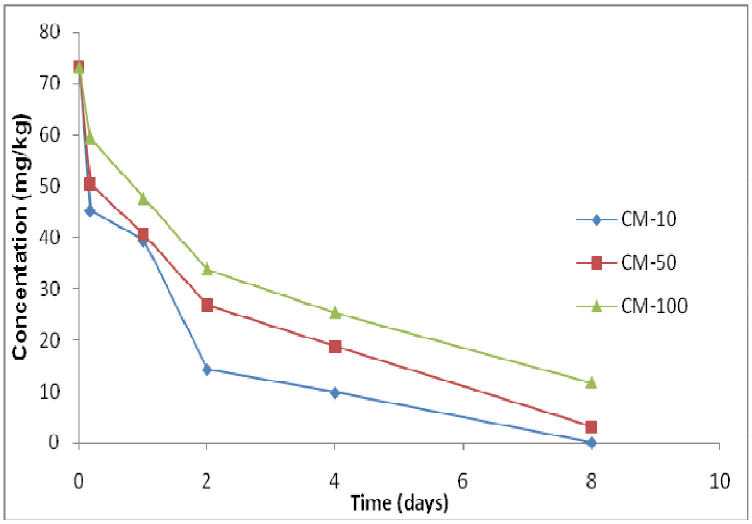

Fig. 2 Effect of concentration of α-cypermethrin on its photodegradation

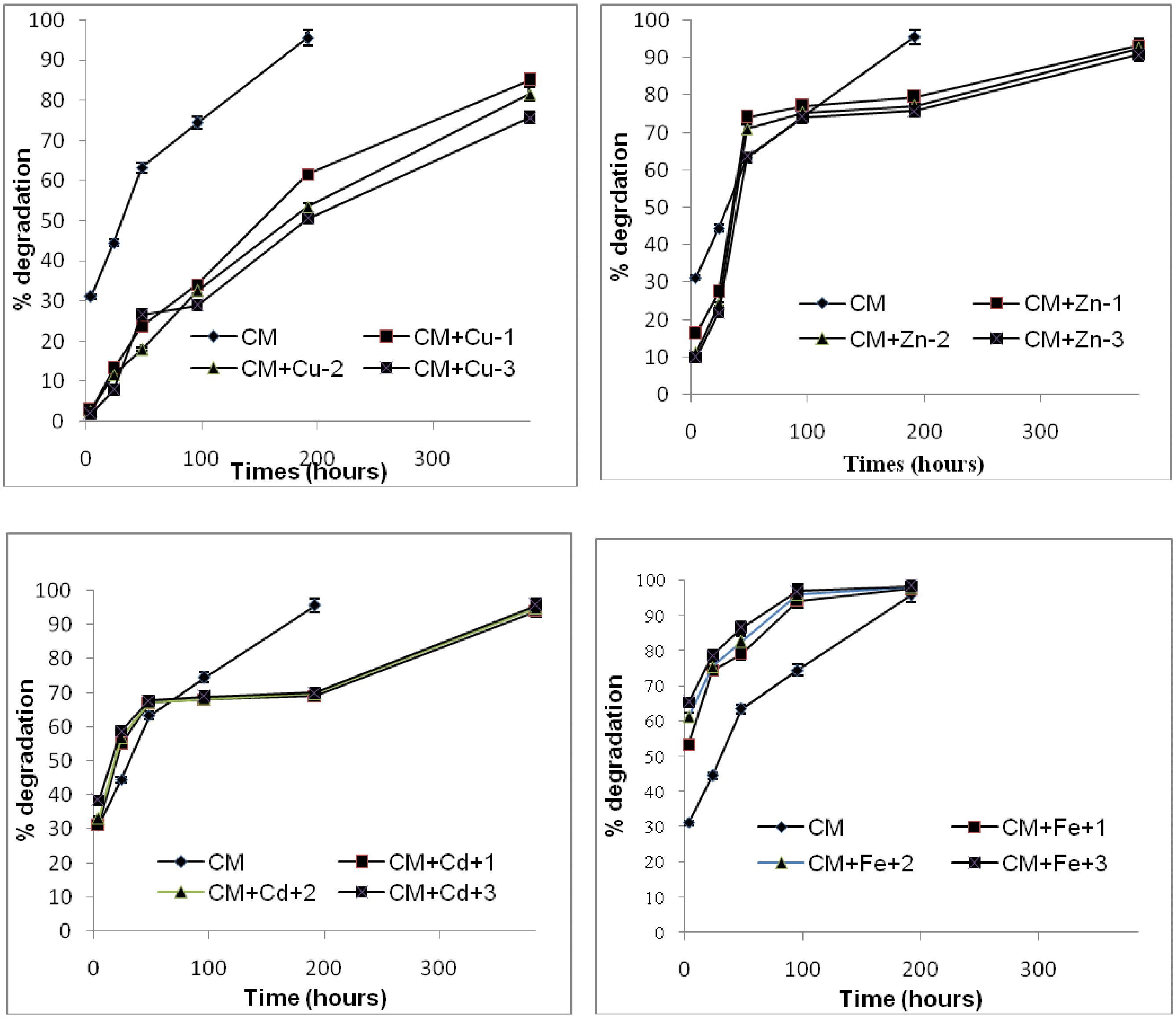

Fig. 3 Effect of metal concentration on Photodegradation of α-cypermethrin

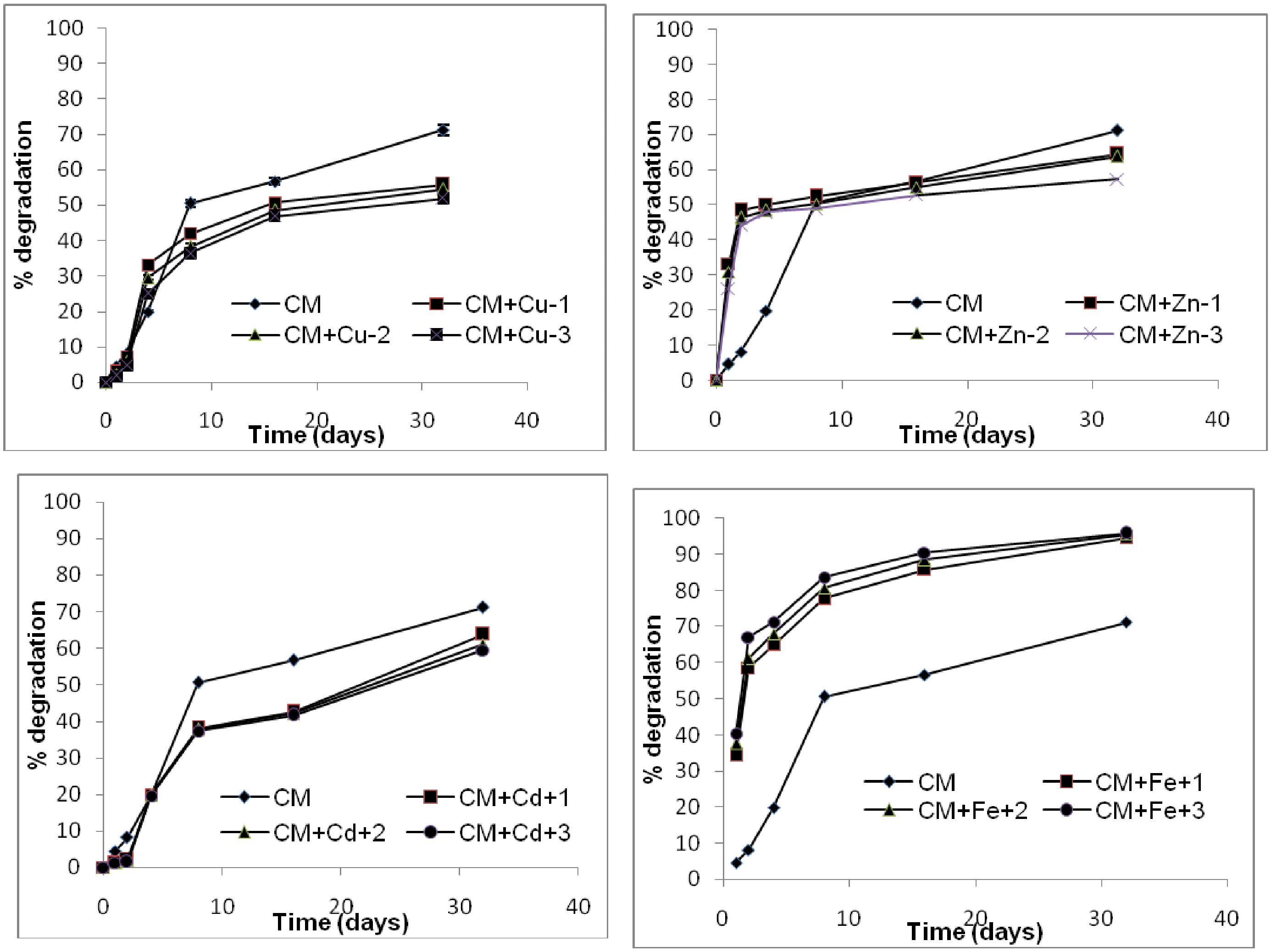

Fig. 4 Effect of metal concentration on microbial degradation of α-cypermethrin

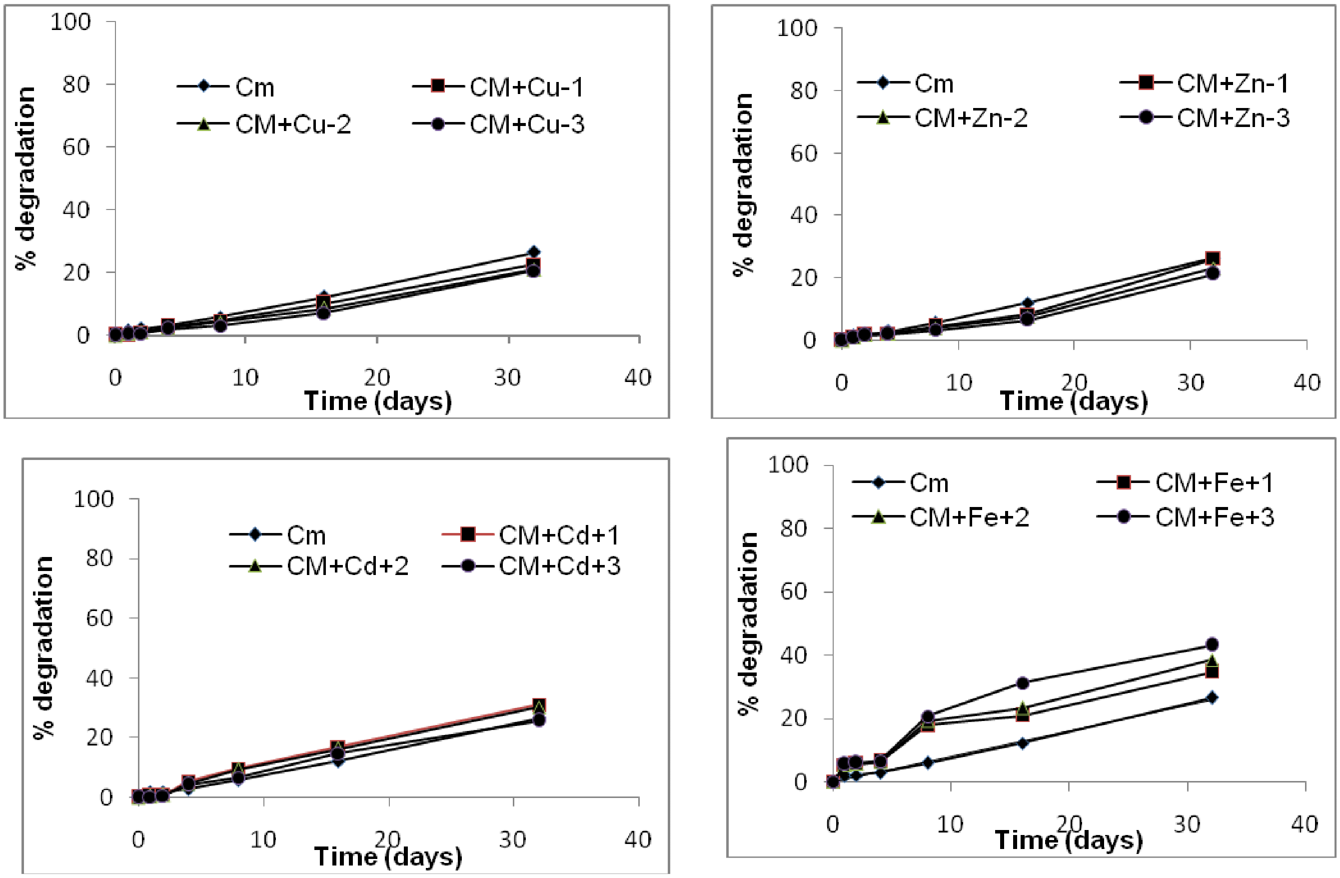

Fig. 5 Effect of metal concentration on abiotic degradation of α-cypermethrin

Tables

Table.1. Elementary properties of the pesticide along with its degradation prolife in soil

Pesticide	**Mol. wt (g)**	**Solubility in water (mg L^{1-})**	**Henry constant**	**Vapor Pressure**	**Application rate (g Ha^{1-})**	**Chemical stability in dark**	**Aerobic /anaerobic transformation in soil**	**Phototransformation soil surface**	**Stable Degradation products in soil**
α-Cypermethrin $C_{22}H_{19}C_{l2}NO_3$	416.3	3.97 (pH=7), **25°C** 1.25(DDW) µg L^{1-} at 20°C[73]	2.5x10-7 atm-m3 /mol[74]	5.1 x 10^{7-} nPa at 70 °C[75] 4 x 10-8 mm Hg at 70 °C[74]	10-15g/ha .	Very stable in neutral and acidic media, hydrolyzed in strongly alkaline media,DT50 (pH 4, 50°C) stable over 10d, (pH 7, 20°C), 101d (pH 9, 20°C) 7.3d[73]	2–8 weeks/ 63 days [73,76]	UV; 56.08 min on clay loam, 94.07 min on loam, sunlight 2.24 d on clay loam, 3.14 on loam[41]	3- PBA[73]

Tomlin 2004[73], Hayes and Laws , 1990[74];Kidd and James, 1991[75]; US Department of Agriculture,1990[76]; [e] Raikwar and Nag 2011[41]

Table 2. Physico-chemical properties of the studied soil

Soil Type	**Soil texture**			**M. C %**	**O.M %**	**pH (1:2)**	**CEC (mmol/ kg)**	**Trace metals (mg/kg)**			
	% clay	**% sand**	**% Silt**					**Fe**	**Zn**	**Cd**	**Cu**
Sandy	4.5	87	8.5	2.34	4.62	7.4	8.3	863	6.9	0.7	15.9

Table. 3 Dissipation statistics of degradation of α-cypermethrin

Pesticide	Environment	Trace metal	Model	k_1(h-)	r^2	t_b (days)	k_2 (h-)	r^2	$t_{1/2}$ (days)
α-Cypemethrin	UV		HS	-1.078	0.686	1	-0.236	0.916	0.64 ± 1.41*
	Dark unsterile		HS	-0.151	0.99	8	-0.046	0.747	33.63 ± 1.92
	dark sterile**		HS	-0.024	0.994	32	-	-	-
	UV	Fe^{2+}	HS	-1.175	0.94	2	-0.024	0.663	0.59 ± 2.07*
	Dark unsterile		HS	-0.925	0.989	2	-0.035	0.855	54.03 ±1.4
	dark sterile**		HS	-0.032	0.936	32	-	-	-
	UV	Zn^{2+}	HS	-0.978	0.945	2	-0.017	0.935	0.71 ± 1.2*
	Dark unsterile		HS	-0.701	0.955	1.2	-0.021	0.697	41.6 ± 2.9
	dark sterile**		HS	-0.022	0.96	32	-	-	-
	UV	Cd^{2+}	HS	-1.397	0.813	1	-0.088	0.734	0.49 ± 2.01*
	Dark unsterile		HS	-0.152	0.84	4	-0.042	0.918	17.7 ± 0.429
	dark sterile**		HS	-0.029	0.991	32	-	-	-
	UV	Cu^{2+}	HS	-0.147	0.937	8	-0.067	0.944	4.7 ± 1.04*
	Dark unsterile		HS	-0.282	0.908	4	-0.024	0.847	49.7 ± 1.12
	dark sterile**		HS	-0.023	0.996	32	-	-	-

* DT_{50} was in hours.

** (t_b not reached till 32 days of study period So, DT_{50} was not possible to calculate accurately by HS model)