



Zn²⁺ and Cd²⁺ assisted photo-catalytic degradation of chlorpyrifos in soil

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ABSTRACT

The Cd²⁺ and Zn²⁺ assisted photo-catalytic degradation of soil incorporated chlorpyrifos (CLP) was reported in current study. The soil samples fortified with CLP and metals were irradiated in photo-reactor for different time intervals to check maximum degradation. Soil samples extracted with acetonitrile were analyzed by HPLC. The results of the study revealed a complete mineralization of insecticide from soil that followed first-order Langmuir-Hinshelwood (L-H) kinetic model. The CLP degradation rate in soil was higher in photoreactor than control with variation in half-life from 41 days to 20 days. The degradation of CLP in photoreactor was 5 fold augmented after Zn²⁺ fortification of soil while Cd²⁺ had negligible effect on CLP photodegradation. Thus Zn²⁺ fortification of soil will not only replenish the important nutrient for plant growth but will also help in alleviating the harmful effects of CLP on soil flora and fauna by enhancing its rate of photodegradation.

1. Introduction

The co-existence of pesticides residues and heavy metals in soil environment is anxious as their simultaneous presence in soil can potentiate their toxicity to soil organisms (Chen et al., 2015), inhibits the activity of the soil enzymes (Mansour et al., 2009), enhance persistence of either (Liu et al., 2007), increased mobility and affect bioavailability to food chain (Bayen, 2012). Although few researchers has been tried to characterize these interactions but their potential cocktail effect and toxicity remains mysterious till now (Reddy et al., 2012; Chen et al., 2015). Metals affect the pesticides degradation in multiple ways either they enhance the pesticides breakdown like Fe and Cu enhanced the degradation of metribuzin, chlorpyrifos, imidacloprid (Vágvölgyi et al., 2010; Reddy et al., 2012; Rafique and Tariq, 2015), modulated its dissipation rate e.g. cobalt, Cd²⁺ and manganese decreased the degradation of organophosphorus pesticide (such as fenitrothion, chlorpyrifos), Copper nanoparticles can increase the persistence of Atrazine in soil (Moon, 1990a,b, Parada et al., 2019) and unaffected the pesticides dissipation rate like nickel unaffected the degradation of metribuzin (Moon, 1990a,b) and Pb had little influences on the dissipation of high concentrations atrazine (Chen et al., 2014).

The repeated use of chlorpyrifos (CLP) for eradication of pests from cotton, wheat and vegetable fields has increased the public concerns on potential human health risks. Several reports indicate the presence of CLP

in soil, crops, grains and blood of farmers around the world (Mansour et al., 2009, Rafique et al., 2016a,). Excessive use of fertilizer, organic manure and waste water for irrigation is main source of heavy metals in these soils (Rafique et al., 2016b).

CLP degraded in the soil environment by chemical degradation, photolysis and photo-induced degradation and biodegradation (Reddy et al., 2012) Although microbial dissipation is primary metabolic pathway for its soil dissipation, yet the process is inefficient due to accumulation of antimicrobial degradation product 3, 5, 6, trichloro-2-pyridinol (TCP) (Robertson et al., 1998; Fernández-Alberti et al., 2012). Moreover continuous addition of chlorpyrifos to the soil resists the microbial population ability to degrade this pesticide dissipation in soil. When it is exposed to UV or sunlight, it dissipated either by hydrolysis, de-chlorination or oxidation. The metabolic products are unstable hence does not accumulate in the soil (Jabeen et al., 2015).

Heavy metals may influence the degradation of pesticides in two ways, i.e. they may reduce it or enhance it. For example, Zn²⁺ and Cu²⁺ are known to reduce the dissipation of deltamethrin and cypermethrin in the soil but Fe promotes their dissipation rate (Yang et al., 2010). Similarly, our previous studies have also reported the degradation of CLP, and a number of other pesticides in the presence of some metals (Rafique et al., 2016a, Rafique and Tariq, 2015). It is important to determine the metals that have pronounced influence on the photodegradation of pesticides but have minimal hazardous effect on the environment so that a

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strategy may be developed for safer remediation of these pesticides from the soil. So, present study was designed to determine the influence of Cd^{2+} and Zn^{2+} ions on the dissipation of CLP in the soil.

2. Materials and methods

2.1. Chemicals

Analytical-grade standard of Chlorpyrifos (>99% purity) was purchased from Sigma-Aldrich, (Steinheim, Germany). The physico-chemical properties of chlorpyrifos are tabulated in Supplementary Table 1. Pesticide stock solutions (1000 mg L^{-1}) were prepared in HPLC grade methanol (Merck) and were stored in dark at -20°C . LC grade acetonitrile, methanol, spectroscopic grade anhydrous magnesium sulfate, zinc chloride and cadmium chloride were purchased from Sigma-Aldrich. Deionized water for current experiment was prepared with a Milli-Q system from Millipore-Waters Co. (Bedford, MA).

2.2. Soil collection and characterization

Surface soil sample of cotton tunnels were collected from National agricultural research council (NARC, Pakistan) at a depth of 20 cm and used for the present study. The physico-chemical properties of the collected soil sample were carried out by Land Resource Research Institute, (NARC, Pakistan) and are summarized in Supplementary Table 2. The soil free of pesticides was prepared by stirring the soil sample with acetone for 24 h thrice, decanting and drying at room temperature. This sample was then dried in an oven at 105°C and passed through 2 mm sieve. A 75% water holding capacity (WHC) of soil sample was maintained by adopting the method of Frank et al. (Frank et al., 2002) and then stored at 20°C in dark. Soil sample were sterilized by autoclaving for 2 h at 121°C (Razavi Darbar and Lakzian, 2007).

2.3. Spiking procedure

The spiking solution of $50 \text{ }\mu\text{g/mL}$ concentration was prepared by dilution of standard CLP solution prepared at a concentration of $500 \text{ }\mu\text{g/mL}$ in acetonitrile. For metal assisted degradation tests, CdCl_2 and ZnCl_2 stock solutions were prepared at concentrations of 1000 mg L^{-1} . Soil samples were spiked with CLP at the maximum field concentration of $0.5 \text{ }\mu\text{g/g}^{-1}$. The final concentrations of Zn^{2+} was 27 (control treatment), 37, 47 and 57 mg kg^{-1} and that of Cd^{2+} were 0.8 (control), 10.8, 20.8 and 30.8 mg kg^{-1} as confirmed by atomic absorption spectrophotometer after digestion with $\text{HNO}_3/\text{H}_2\text{SO}_4$.

2.4. Photo-irradiation experiment

Photo-degradation experiment was carried out in self-designed photoreactor, having 8-W UV tubes (Atlas, Linsengericht, Germany) (used for irradiation of the soil samples). To control temperature and water circulation system, fan is fitted inside the radiation chamber. Spiked and reference unspiked soil samples were irradiated for specified time interval. Initial moisture level of soil samples were maintained during the experiment period (Rafique and Tariq, 2015).

The soil slurry (prepared by 10.0 g of soil (dry weight) mixed with 7.5 mL of water) was spiked with $100 \text{ }\mu\text{L}$ of pesticide spiking solution. Control samples were spiked separately with 1 mL of Cd^{2+} and Zn^{2+} spiking solution. The spiking solutions were dispensed via micro-syringe. The soils samples after thorough mixing and uniform distribution were irradiated in the photo-reactor for different time intervals. Each experiment was carried out in triplicate under destructive sampling mode. The control experiments without pesticide and heavy metals addition were carried out concurrently. To eliminate the role of biodegradation and hydrolysis control sterilized (autoclave at 121°C for 2 h thrice) and unsterilized soil samples under dark conditions were analyzed along with irradiated samples.

2.5. Pesticide extraction and analysis

Extraction of irradiated soil samples was carried out with acidified acetonitrile (0.1% glacial acetic acid) for analysis of CLP residues in soil. Briefly, soil samples were extracted thrice with acidified acetonitrile, vortexed for 1 min and sonicated for 15 min in ultrasonic bath (100 H , $80/160 \text{ W}$ Sonorex, Germany). After extraction, combined extract (ca. 30 mL) was passed through anhydrous sodium sulfate and concentrated in rotary evaporator (R-210). The concentrated extract was passed through florisil column prepared by packing with glass wool, 2 g MgSO_4 , 1 g florisil and 2 g MgSO_4 . The column was pre-conditioned with acetonitrile and eluted with 10 mL of acidified acetonitrile. The eluents were evaporated under gentle stream of nitrogen and re-constituted in acetonitrile. The extraction method was efficient and reproducible with mean recoveries of $84\text{--}101\%$ with relative standard deviations of lower than 1.2% for whole procedure (Gilani et al., 2010).

The identification and quantification of CLP residues in soil samples were carried out by HPLC, Agilent 1100 system equipped with ultraviolet detector and Eclipse XDB-C18; size: ($250 \text{ mm} \times 4.6 \text{ mm} \times 5 \text{ }\mu\text{m}$). The mobile phase consisting of acetonitrile and acetate buffer ($90/10$, v/v) was used for chromatographic separation with a flow rate of 1.0 mL/min and detected at λ_{max} 290 nm with injection volume of $2 \text{ }\mu\text{L}$. Under the above conditions, R_t of CLP was 6.7 min and LOQ was $0.05 \text{ }\mu\text{g/mL}$. Calibration curve with regression coefficient of $0.999 (\pm 0.04)$ ($n = 6$) was used for quantification by using external standards (Zalat et al., 2014).

2.6. Metal speciation studies in soil

Modified Tessier's scheme was used to study the speciation of selected metals in agricultural soil which was important to determine the role of metal in dissipation of pesticides. According to this scheme, the metals in soil are distributed among five different fractions such as carbonate bound, water soluble, exchangeable, organic fraction and residual fraction by using different reagents.

2.7. Data analysis

The data for the photodegradation of CLP in the soil was studied by fitting the Langmuir-Hinshelwood (L-H) model

$$\ln(\text{Co}/\text{Ct}) = -k't$$

Where k = first-order rate constant (time^{-1}) (Konstantinou and Albanis, 2003). The $t_{0.5}$ of pesticide is determined by the equation.

$$t_{0.5} = (1/k) \ln 2.$$

3. Results and discussion

3.1. Photodegradation studies of soil amended with CLP

Photo-transformation is an environmental friendly pathway for CLP dissipation in soil as its photodegradation products are unstable hence does not accumulate in the soil (Walia et al., 1988; Jabeen et al., 2015). Experiments were carried out to check the influence of direct artificial light (UV tube and visible by Hg vapor lamp) and natural sunlight on the dissipation rate of CLP. The UV-induced photodegradation rate of soil incorporated CLP was found to be $3.5 \times 10^{-2} \text{ day}^{-1}$ with $r = 0.988$. This rate was faster than direct sunlight and visible light. The half life ($t_{0.5}$) of the pesticide was reduced to 20 days from 36 days under UV irradiation (Table 1). This observation was explained on the basis of facts that UV rays had short-wavelength and high energy thus they easily initiated the photodegradation of organic compounds like CLP (Muhamad, 2010).

The dissipation half life ($t_{0.5}$) of CLP was recorded to be 31 days in unsterilized treatments, which was slow due to accumulation of

Table 1

Dissipation statistics of degradation of chlorpyrifos contaminated soil amended with trace metals.

Pesticide	Cultivation environment	Trace metal	k	t _{1/2} (days)	r ²
Chlorpyrifos (50 mg kg ⁻¹)	UV		3.5×10^{-2}	19.80 ± 2.31	0.988
	Dark unsterile		2.3×10^{-2}	30.13 ± 1.13	0.992
	Dark sterile		1.7×10^{-2}	40.76 ± 0.96	0.997
	UV	Zn ²⁺	1.58×10^{-1}	4.39 ± 0.36	0.983
	Dark unsterile		5.9×10^{-2}	11.74 ± 0.76	0.984
	Dark sterile		3.1×10^{-1}	23.1 ± 0.49	0.937
	UV	Cd ²⁺	3.6×10^{-1}	19.25 ± 2.15	0.999
	Dark unsterile		2.4×10^{-1}	28.9 ± 1.21	0.983
	Dark		2.1×10^{-1}	33 ± 1.14	0.996

antimicrobial TCP (3, 5, 6-trichloro-2-pyridinol, Fig. 1) as was also described by Menon et al. (2004). The degradation of CLP was very slow in the dark sterile soil conditions with a rate constant being 1.7×10^{-2} and a t_{0.5} that was half than that under UV irradiation (Fig. 1). These dissipation study results are in well agreement with the results obtained by other researchers (Singh et al., 2002; Rokade and Mali, 2013; Jabeen et al., 2015). In the absence of any light (dark) and microorganisms (sterile), hydrolysis was described as the main process that caused the dissipation of CLP in the soil. Racke et al. (1996) also observed a slow dissipation of CLP under sterile conditions in alkaline soils (Racke et al., 1996).

Concentration of CLP has inverse relationship with its

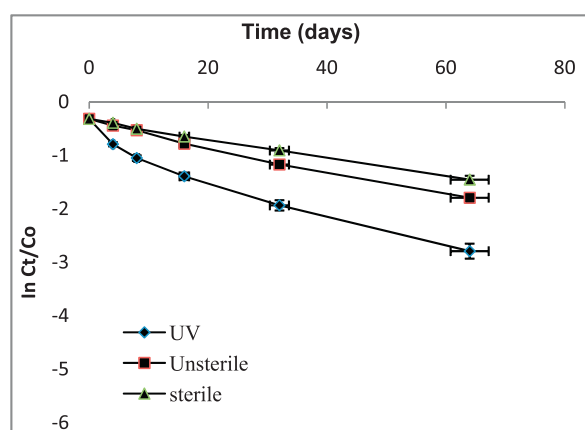
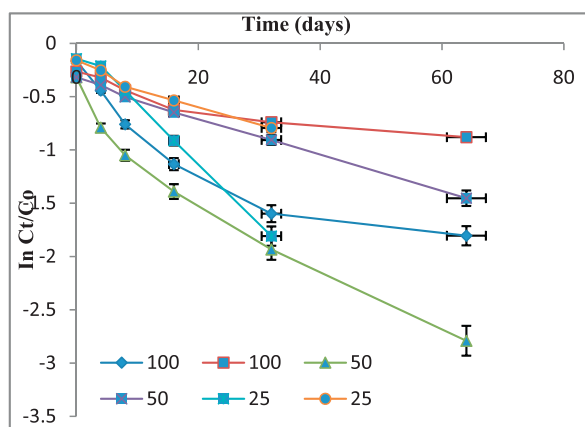
**a****b**

Fig. 1. a. Degradation profile of chlorpyrifos in soil. b. Effect of Initial conc on chlorpyrifos on its dissipation in soil.

photodegradation efficiency i.e. an increase in initial concentration of CLP in soil was observed to be associated with a decrease in its photodegradation rate and vice versa [Fig. 1-b]. A Similar relation has already been reported by Rafique et al. (2016a, as well as by Racke et al. (1996), where the degradation rate of 1000 µg/g was much retarded than 10 µg/g of initial concentration. It is clear from the curves that maximum degradation takes place in the early stage (10days) and the remaining part of pesticide takes much longer time for removal due to the formation of intermediates. This observation is also supported by Sivagami et al. (2014)).

3.2. Metal speciation studies in soil

Speciation of metal in agricultural soil helps in deciding the role of metal in breakdown of pesticide. The distribution of the metals in various operationally defined fractions in surface soil evidenced that Cd and Zn are mostly associated to organic fraction. The appreciable concentration of Zn was also present in water soluble and exchangeable fractions respectively. The organic matrix of the soil has the advantage of having most of the adsorbed pesticide in it. So if a metal is associated with this matrix, it may be expected to enhance the degradation of pesticide as metal may absorb energy from UV radiations and easily transfer it to adsorbed pesticides thereby facilitating its degradation. But at the same time, organic matrix also causes the agglomeration of clay particles that may hinder the light reaching the metal and hence a reduction in rate of photo-degradation may be observed.

3.3. Impact of Zn²⁺ addition on CLP photodissipation

The photodegradation rate of CLP was observed to increase from 3.5×10^{-2} to 1.6×10^{-1} when soil samples were augmented with Zn²⁺ resulting in a rapid decrease in t_{1/2} from 20 to 4.4 days (Table 2). The photodissipation rate was directly correlated with soil Zn²⁺ content. The huge variance in reaction rate of UV and dark incubation reaction pointed toward the fact that photodegradation was the main degradation pathway during remediation of CLP contaminated sites. Zn²⁺ also enhanced the dissipation rate from 2.3×10^{-2} to 5.9×10^{-2} with a decrease in t_{1/2} from 30 to 12 days (Fig. 2-a). There is a positive correlation between soil Zn content and soil metabolic quotient and negative correlation with carbon microbial biomass, microbial biomass, nitrogen and the microbial quotient (Kamitani et al., 2006). Photodegradation of CLP was enhanced with significant reduction in t_{0.5} from 41 to 23 days when soil Zn content increased even under the dark sterile conditions at p > 0.05 (Fig. 2-a). Zinc has also been reported to enhance the photodegradation of α-cypermethrin in soil (Rafique and Tariq, 2015).

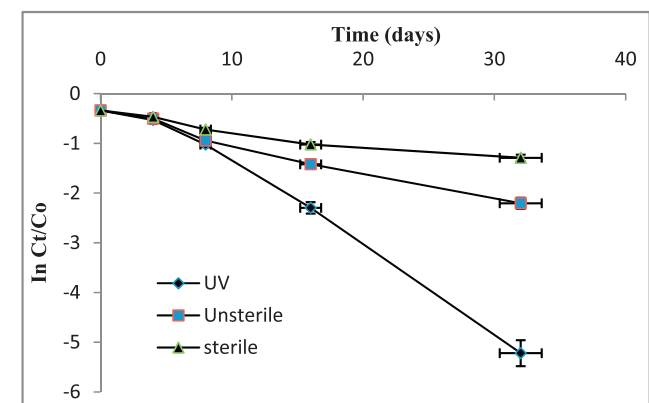
3.4. Effects of Cd²⁺ on CLP photodegradation

Cd²⁺ slightly augmented the photodegradation of CLP with reduction

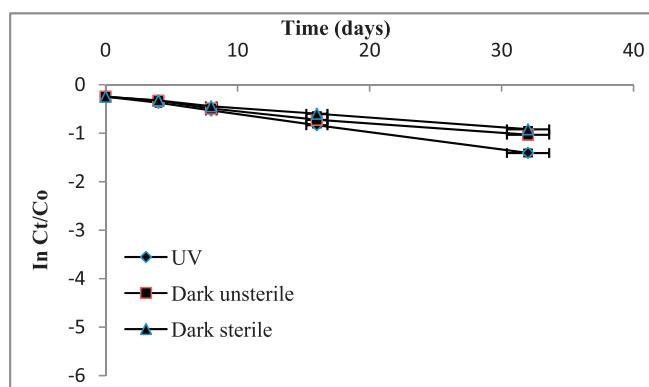
Table 2

Dissipation statistics of soil contaminated with chlorpyrifos amended with different Zn²⁺ and Cd²⁺ levels.

Pesticide	Cultivation environment	Trace metal	Metal conc.	k	t _{1/2} (days)	r ²
Chlorpyrifos	UV	Zn ²⁺	20	1.59×10^{-1}	4.39 ± 0.36	0.983
			40	1.65×10^{-1}	4.20 ± 1.64	0.985
			80	1.81×10^{-1}	3.83 ± 1.91	0.989
			100	1.81×10^{-1}	3.83 ± 1.91	0.989
		Cd ²⁺	10	3.6×10^{-2}	19.25 ± 2.15	0.999
			20	5.2×10^{-2}	13.32 ± 0.83	0.983
			40	7.4×10^{-2}	9.36 ± 1.43	0.994
			100	1.6×10^{-1}	4.4 ± 0.36	0.983



a



b

Fig. 2. a. Degradation profile of chlorpyrifos in Zn^{2+} amended soil. b. Degradation profile of chlorpyrifos in Cd^{2+} amended soil.

in $t_{1/2}$ from 20 to 19 days when soil Cd^{2+} content was low (10.8 mg kg^{-1}) but dissipation rate was enhanced with the reduction in $t_{1/2}$ from 19 to 9.4 days with increase in soil Cd concentration from $\text{C}^0 + 10 \text{ mg kg}^{-1}$ to $\text{C}^0 + 40 \text{ mg kg}^{-1}$ (Table 2, Fig. 2-b). Cd based photocatalysts were used by Barakat et al. (2014) for the elimination of methomyl from soil (Barakat et al., 2014). Degradation rate of CLP in unsterilized control was low at $p < 0.05$ as microflora is extremely sensitive to cadmium (Fig. 2-b). The microbial activity of certain pesticides degrading bacterial strain is known to be stumpy even at low Cd concentration in soil. Li, Zhou et al. (2011) observed that activity of *Variovorax* and *Rhodococcus* strains to degrade carbendazim and diuron was impeded in the presence of Cd (Li et al., 2011). Dissipation $t_{0.5}$ of CLP in soil amended with Cd^{2+} in dark sterile control was decreased from 41 days to 33 days evidencing that Cd^{2+} enhanced its chemical degradation even in the absence of light (Fig. 2-b).

3.5. Proposed degradation mechanism

Pesticide mostly photodegraded either by redox reaction mechanism or free radical mechanism. While metals mostly affect degradation of pesticides either by oxidation and hydrolysis or nucleophilic substitution reactions (Bootharaju and Pradeep, 2012). In both cases, two major metabolites of chlorpyrifos are, 3, 5, 6-trichloro-2-pyridinol (TCP) and diethyl triphosphate (Walia et al., 1988). The divalent metal (Zn and Cd) can bind with sulfur and nitrogen atoms to form a surface complex, as they have a lone pair of electrons. The formation of the Metal $n + \leftarrow \text{S}$ bond is reported by Bootharaju and Pradeep (2012) for Ag mediated degradation (Bootharaju and Pradeep, 2012).

4. Conclusions

The results of the study revealed that photo-degradation of CLP has linear relationship with soil Zn^{2+} and Cd^{2+} content. The initial concentration of pesticide was inversely related with the rate of photo-degradation. Both the studied metals i.e. Zn^{2+} and Cd^{2+} influenced the abiotic degradation of CLP. Zn^{2+} exhibited a pronounced effect in photodegradation of CLP resulting in the $t_{0.5}$ reduction from 20 to 4.4 days which was found to be 9.4 days in case of cadmium. The microbial degradation of CLP in soil was also enhanced by the presence of Zn^{2+} content while Cd^{2+} exhibited only negligible effect on it. Thus Zn^{2+} amendment under UV irradiation may help in remediating the soil contaminated with chlorpyrifos.

Declarations

Author contribution statement

Nazia Rafique: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Saadia Tariq: Conceived and designed the experiments; Wrote the paper.

Karam Ahad: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Fahad Rafique: Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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