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Effect of Soil Physicochemical Properties on Adsorption of Tricyclazole

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Abstract

Many processes affect the behavior of pesticides in the environment, namely adsorption, transfer, breakdown and degradation. Adsorption-desorption are a dynamic process in which molecules are continually transferred between the bulk liquid and solid surface. Adsorption-desorption of pesticides in soils depend upon various factors like soil pH, CEC, clay content, organic matter and metal oxides. Tricyclazole (5-methyl-1,2,4-triazolo[3,4-b]benzothiazole), a systemic fungicide, used to control the rice blast in paddy cultivated in India. Adsorption studies were conducted in three soils having varied physicochemical properties. The pH of the soils varied from 5.3, 8.1 and 8.5 in alfisol of Raipur, inceptisol of Delhi and inceptisol of Karnal, respectively. The adsorption studies were carried out in triplicate at initial concentrations of 5,10,15,20 and 25 μg/mL of tricyclazole. All the concentrations were below the solubility of pesticide in water. The adsorption studies were carried out at 1:5 ratios of soil and water. The samples were analyzed by HPLC fitted with Rp-18 column and PDA detector at λ_{max} 230 nm. The lowest adsorption of tricyclazole occured in Karnal soil (46.78-33.98 %), and highest adsorption occurred in Raipur soil (61.92-50.26%). Kf_{ads} (Freundich) values of tricyclazole were 9.68, 7.92 and 6.18 mL/g in Raipur, Delhi and Karnal soil, respectively. Tricyclazole is strongly adsorbed in Raipur soil as compared to soils of other regions as indicated by the highest Kf_{ads} value. The corresponding Kd values for the adsorption process were 6.61, 5.08 and 3.67mL/g, for Raipur, Delhi and Karnal, respectively. The results revealed that adsorption is influenced by soil physicochemical properties, and showed that the maximum adsorption of pesticide was observed in soils with higher organic carbon, clay content and low soil pH.

1. Introduction

Tricyclazole (5-methyl-1,2,4-triazolo[3,4-b][1,3]benzothiazole), is a systemic fungicide, belonging to triazolobenzothiazole class of compounds (WHO, 2005). It is used mainly as a protectant, curative, eradicant and for control of disease by inhabitation of melanin biosynthesis. Tricyclazole controls powdery mildew, rusts and *Rhynchosporium* in cereals when applied as a seed treatment. It is effective for the control of bunt, smuts, seedling blight, leaf stripe, net blotch and other cereal diseases (Padovani etal., 2006; Phong et al., 2009a; Phong et al, 2009b) Phong TK .In India It is mainly used for the control of rice leaf blast and rice panicle blast. In India there is scare information regarding the environmental fate of tricyclazole in soils of rice growing regions of India. In view of the above we propose to study the adsorption behavior of tricyclazole in soils having different physicochemical properties.

2. Methodology

2.1 Soil samples

Fresh soil samples were taken from three soil samples were collected from three different agricultural areas, representing a range of physicochemical properties. Subsamples of homogenized soils were analyzed for organic matter content, particle size distribution, texture, pH. **Soils taken were from IARI research field (Delhi soil, Inceptisol), Raipur (Alfisol) and** Karnal (Inceptisol). The soil characteristics are given in Table 1.

2.2 Chemicals

Commercial formulation of tricyclazole Force 11® 75% WP was obtained *gratis* from Insecticide India Pvt Ltd. All the solvents used were glass distilled before use**.** Single distilled and double distilled water was used for the experiment. HPLC grade acetonitrile and Millipore water were used for HPLC analysis. All the solvents were filtered through 0.45 µm filter and sonicated before use. The adsorbents and drying agents were activated for four hours at 100^{o}C before use. HPLC analysis was carried out on Shimadzu HPLC system with LC -19 AT VP with system controller SCL-10A VP, dual pump FCA -10Al VP, degasser DGU 14A, fitted with Diode array detector SPD-M 10A VP, autosampler SIL-10A DVP and column oven CTO-10 AS VP

2.3 Determination of equilibration time

2 gm soil was taken in each of the ten test tubes and 10 mL of 5 µg/mL of aqueous solution of tricyclazole was added. The test tubes were placed on mechanical shaker for shaking for different time intervals. The test tubes were taken out at each sampling time after 1, 2, 4, 6 and 24 hours of shaking. The tubes were centrifuged at 2000 rpm for 10 minutes. The supernatant solution (8 mL) was drawn without disturbing the soil. The supernatant solution was extracted similar to aqueous samples and analyzed residues using HPLC. A blank sample without soil was used as control to observe any sorption/degradation of tricyclazole the glass surface.

2.4 Adsorption studies

Adsorption study was carried out using batch equilibration technique. The adsorption studies were carried out in triplicate at initial concentrations of 5,10,15,20 and 25µg/mL of tricyclazole. All the concentrations were below the solubility of pesticide in water. 2 gm of selected soils were taken in ground glass joint test tubes (50 mL capacity) and 10 mL of aqueous solution tricyclazole was added. The tubes were stoppered and shaken for 6 hours at room temperature and then centrifuged at 2000 rpm for 10 minutes. After centrifugation, clear supernatant solution (8 mL) was transferred to a separatory funnel, diluted with aqueous sodium chloride solution (10% 20 mL) and then extracted by partitioning with dichloromethane (3 x 30 mL). The organic phase was passed through anhydrous sodium sulfate and concentrated to dryness in a rotary evaporator. The residues were dissolved in known quantity of acetonitrile and analyzed by HPLC.

2.5 Calculation and Data Analysis

$\text{Log } C_s = \log K_F + 1/n \log C_e$

Cs is adsorption of pesticide on soil surface, (Ce) is the equilibrium concentration in solution and K_F is Freundlich adsorption coefficients and n is a linearity factor, it is also known as adsorption intensity. 1/n is the slope and log K_F is the intercept of the straight line resulting from the plot of log Cs versus log Ce as shown in table 3.

3. Result and Discussion

3.1 Equilibration Time

The maximum recovery was obtained after 6 hours, and change in adsorbed amount was negligible (Fig 1).

3.2 Adsorption study

The highest adsorption of tricyclazole was observed in the alfisol of Raipur soil followed by Delhi soil and Karnal soil, respectively. In general the adsorption percentage was lower at the higher concentrations of tricyclazole (Table 2) and this is reflected in the 1/n values, which are less than 1.0 (Table 3), illustrating that adsorption is nonlinear with respect to concentration (Figure 2). This kind of isotherm arises because of minimum competition of solvent for sites on the adsorbing surface. The slope of the isotherm steadily decreases with the rise in solute concentration because vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm indicate that the number of available sites for the adsorption become a limiting factor. This may be due to the possibility that the fungicide molecules occupy most of the adsorption sites at the higher concentrations. The adsorption of pesticide in high organic matter soil (Raipur soil) was more than other soils. This increase could be related to the sorption of organic matter to the soil by increasing the sorption sites available for adsorption. The interaction between pesticide and organic manure occur via multiple bonding mechanisms including ionic bond

between negative charged organic matter and positively charged pesticides and/or hydrogen bonds in between pesticides and organic matter as (Durovic et *al.*, 2009) The K_{fads} values observed for the Raipur soils suggested that the higher adsorption of tricycalzole to soil could be attributed to the high OM, clay content and low pH of soil. Similar observation was recorded by Li *et al*. (2003). Freundlich coefficient K_F for Raipur, Delhi and Karnal soils were 9.68, 7.92 and 6.18mLg^{-1}, respectively for adsorption processes. The values of Freundlich adsorption coefficient (K) was significantly positively correlated with soil organic matter and negatively correlated with soil pH for tricyclazole on all the three studied soils. The values of Kd (distribution Coefficient) [Kd = Cs /Ce] were 8.13-5.05; 6.19-3.88; 4.39-2.57 for alfisol of Raipur, inceptisol of Delhi and inceptisol of Karnal respectively, confirming the above inferences (Figure 3).

Table 1: Physiochemical properties of three soils.

Taxonomical name	Regions	pH	%OC	Texture class	Sand %	Clay %	Silt %
Inceptisol	Karnal (Haryana)	8.4	0.35	Sandy loam	60	10	30
Inceptisol	New Delhi (Delhi)	8.1	0.45	Sand Clay loam	49.0	24.0	27.0
Alfisol	Raipur (Chhattisgarh)	6.3	0.61	Clay loam	30	30	40

Table 2: Percentage of tricyclazole adsorbed onto three soils.

Initial concentration (µg/mL)	Adsorption (% of initial concentration)		
	Alfisol of Raipur	Inceptisol of New Delhi	Inceptisol of Karnal
5	61.92	55.34	46.8
10	58.58	53.38	45.6
15	56.92	50.61	43.3
20	55.46	47.37	40.1
25	50.26	43.75	33.8

Table 3: Freundlich adsorption coefficient of tricyclazole in three soils.

Taxonomical unit	$1/n_{ads}$	Kf_{ads}	Kd	Adsorption %
Alfisol (Raipur)	0.771	9.68	6.61	61.92-50.26
Inceptisol (Delhi)	0.754	7.92	5.08	55.34-43.75
Inceptisol(Karnal)	0.733	6.18	3.67	46.78-33.98

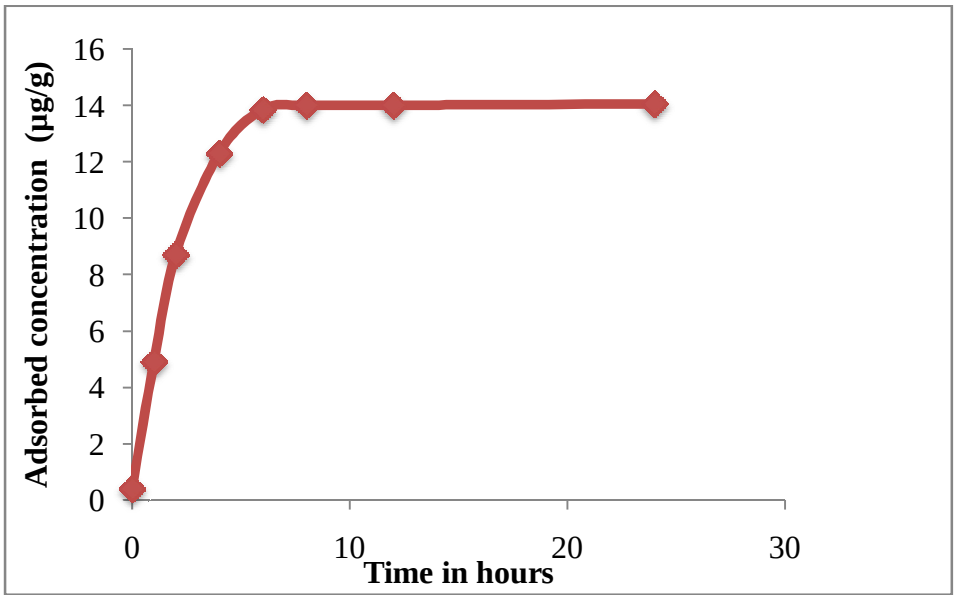

Figure 1: Equilibration time.

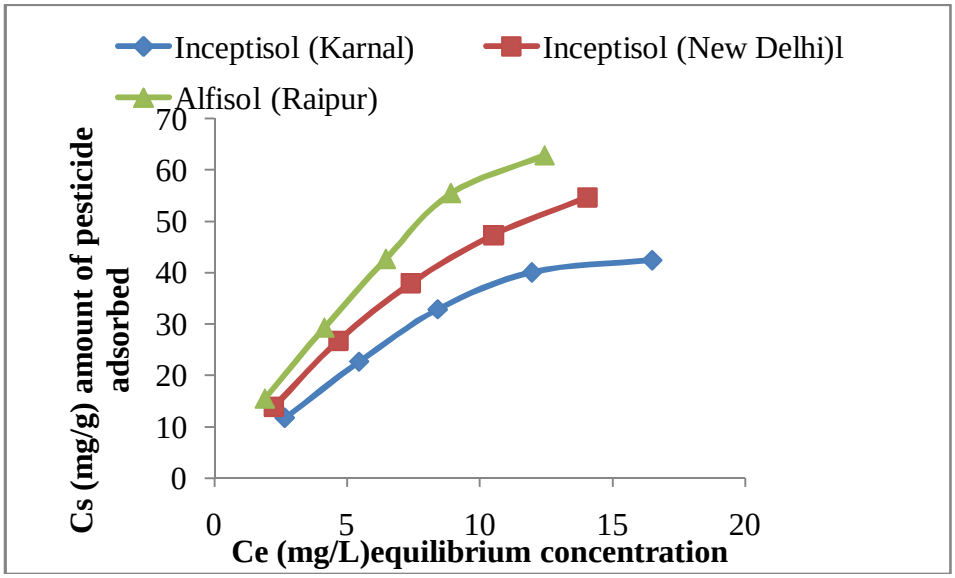

Figure 2: Effect of physicochemical properties on the adsorption.

4. Conclusion

The results indicate that the soil physicochemical properties like soil, pH and organic matter, and play a significant role in adsorption of pesticides. The values of Freundlich adsorption coefficient (K) was significantly positively correlated with soil organic matter and negatively correlated with soil pH for tricyclazole on all the three studied soils. The values of Kd (distribution Coefficient) were 8.13-5.05; 6.19-3.88; 4.39-2.57

for alfisol of Raipur, inceptisol of Delhi and inceptisol of Karnal respectively, confirming the above inferences.

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