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Assessment of Fate of Thiodicarb Pesticide in Sandy Clay Loam Soil

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Abstract

In present study the fate of thiodicarb pesticide in sandy clay loam soil was investigated through its adsorption and leaching using HPLC. Experimental results revealed that thiodicarb follows first order kinetic with rate constant value of 0.711 h^{-1} and equilibrium study showed that Freundlich model was best fitted with multilayer adsorption capacity 3.749 mol/g and adsorption intensity 1.009. Therefore, adsorption of thiodicarb was multilayer, reversible and non-ideal. Leaching study has indicated intermediate mobility of thiodicarb with water due to its solubility, while field study showed the non-leacher nature. However both adsorption and leaching were heavily affected by soil characteristics. As the soil taken was sandy clay loam hence due to clay texture adsorption was higher because of vacant sites existing and greater surface area. For this the pesticide has remained adsorbed in above 20 cm soil layer as clearly seen from field study, minor amount was recorded in third layer of soil having 21-30 cm depth. The leached amount of thiodicarb in first and last part of water was 1.075 and 0.003 ng/µl. The general trend observed for adsorption in column and field soil was decreased downwards from 2.027 to 0.618 and 5.079 to 0.009 ng/µl.

Keywords: Thiodicarb; Adsorption; Leaching; Soil characteristics

Introduction

Carbamate pesticides are frequently used in current era because of their broad spectrum action, fast vanishing rate and normally low mammalian toxicity as compared to other pesticides [1, 2]. But these pesticides are toxic for human beings due to acetyl cholinesterase inhibiting activity [3]. Thiodicarb (IUPAC: 3,7,9,13-tetramethyl-5,11-dioxa-2,8,14- trithia-4,7,9,12-tetra azapentadeca-3,12-diene-6,10-dione) is a carbamate pesticide comprising basically of two methyl moieties joined by sulfur to their amino nitrogen. It acts as an insecticide and molluscicide to control lepidopterous pests, larvae, eggs, chewing and sucking insects, cotton bollworms and budworms, spreading baits for slugs and snails, Coleopterous and some Hemipterous insect pests. It possesses larvicidal and ovicidal actions due to stomach poison hence giving active control when crop growth slackens in the end of the season [4]. This pesticide is used in seed treatment plants and for the control of various pests in cotton, soybeans, tomatoes, peanuts, corn, table, wine grapes, cereals, sweet corn, cole crops, ornamentals, leafy vegetables and other minor use sites [5]. It is neurotoxic initiating metabolic disturbances by obstructing the acetyl cholinesterase in insects and warm blooded animals causing paralysis followed by death. It is a class II category compound (moderately toxic) Group B2 - probable human carcinogen as established by the United States Environmental Protection Agency and World Health Organization [6].

Thiodicarb does not emerge to be very persistent; it possesses low to high leaching potential. From literature it was known that

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thiodicarb had little mobility in clay, intermediate mobility in silt, and high mobility in sand [7, 8, 9]. During hydrolysis, photolysis, metabolism, microbial degradation and alkaline pH, thiodicarb pesticide was degraded rapidly into methomyl. Methomyl is more persistent, more mobile and more toxic than parent [10]. Different methods have been reported in literature for determination of thiodicarb using square-wave voltammetry [11, 12] and HPLC [13, 14, 15, 16, 17]. In these HPLC methods the retention time for thiodicarb was reported as 15.92, 37 and 8 minutes.

The main purpose was the assessment of fate of thiodicarb pesticide in sandy clay loam soil which included the development of greener hplc method and systematic evaluation of adsorption, leaching and pesticide residue in soil.

Materials and Methods

Chemicals

Thiodicarb standard of high purity (99.5 %) was gifted by Bayer Crop Science and commercial thiodicarb was obtained from local market. The solvents used methanol and dichloromethane were purchased from Sharlau (Barcelona, Spain) with purity of 99.8 % and distill water was prepared in laboratory. All glassware used were supplied by Borosil, India and before every experiment, the glassware were cleaned with distilled water and dried at 110 ◦C for 5 h. Primary solution of standard was prepared in methanol and working solutions were made by diluting the main solution. The solutions were stored under refrigeration (4°C).

Adsorption study

Collection of soil samples

The soil samples were taken from okra experimental field of Agriculture Research Institute, Tandojam prior to pesticide application at 0 to 15 cm depth for column study. Following air-dryness, samples were ground and passed through a sieve of 2 mm size. The characteristics of soil were determined using standard methods given in (Table 1). Soil pH was monitored by Jackson, organic matter by Walkley–Black and texture by hydrometer method.

Adsorption investigation

Kinetic sorption was conducted with 5 g of soil mixed in solution volume of 100 ml standard thiodicarb having concentration 100 µg/l. Orbital shaker was used to shake this mixture for 24 hours at the rate of 150 rpm. Sample volume 5 ml was taken at various periods as 0, 0.25, 0.5, 1, 2, 4, 8, 16, 20 and 24 hours and extracted with 5 ml methanol three times. The aqueous layer was removed; the supernatant was filtered and run on HPLC to know adsorbed pesticide concentration.

For equilibrium adsorption, thiodicarb solutions of variable concentrations were mixed with soil weight 5 g and shaken for 10 hours. Then sample volume 10 ml was centrifuged for 20 min at 2000 rpm, obtained supernatant was extracted and analyzed as stated in kinetic section. To observe the influence of pesticide adsorption on walls of flask, a blank solution was also analyzed. To clearly observe the adsorption behavior of thiodicarb, two concentrations ranges low (0.25, 0.5, 1 and 2 ng/µl) and high (5, 10, 25, 50 and 100 ng/µl) were selected.

Leaching study

Column used in this study was made of PVC having length 30 and internal diameter 6 cm. It contained nylon sheath of 0.60 µm size, wool was kept over nylon to put off soil loss form column. The column was packed with soil, drenched with water and left for the night. After that 5 ppm thiodicarb standard solution was applied to the surface of column and left for a period of 24 hours. Subsequently pesticide was removed with 500 ml distilled water at the rate of 100 ml/h in five parts. Flow rate was controlled using peristaltic pump; the column soil was sectioned in three equal parts after elution to observe pesticide adsorption. In order to check the reproducibility three replicate measurements were taken.

Extraction of samples

Soil weight 20 g was mixed with 40 mL methanol in a 100 mL flask, equilibrated on a rotary shaker for 2 hours and the extract was filtered. The filtrate containing pesticide was concentrated to 5ml under stream of nitrogen for HPLC analysis. All water fractions were mixed with 50 mL dichloromethane in a 250 mL separating funnel. The separating funnel was shaken energetically for 5 minutes to make sure the entire amalgamation of two layers. Following partition of two layers, organic layer having pesticide was collected. Dichloromethane extracts were evaporated to dryness by passing stream of nitrogen and residues were redissolved in 5 ml methanol for analysis of pesticide residue using HPLC.

Field residue analysis

Collection of soil samples

The field for experiment was selected at Agriculture Research Institute, Tandojam in 2012. The area of each plot was 25 x50 m^2. The okra crop received good agricultural practices and thiodicarb was sprayed once at recommended dose. The field had received irrigation water following third day of pesticide spray and soil samples were collected one week after pesticide application from randomly selected sites to variable depths of 0 to 10, 11 to 20, 21 to 30 and 31 to 60 cm. These samples were collected in appropriately labeled polyethylene bags, brought to NCEAC, Jamshoro and placed in a freezer at -20 °C until further analysis.

Extraction of residues

Residues from soil samples were extracted following same method as described above in adsorption study section.

HPLC method development

Thiodicarb analysis was performed by HPLC Hitachi model L-6200 with UV-Vis detector model Hitachi L-4200. The selected wavelength was 234 nm. The solvent composition was methanol and water in ratio 30:70 % using reverse phase C18 inertsil ODS-3 (250 mm × 4.6 mm) column with flow rate of 1 mL/min and injection volume was 10 µL.

Data analysis

Kinetic adsorption data analysis was carried out using pseudo first and second order kinetic models, while Langmuir and Freundlich isotherms used for data analysis of equilibrium adsorption. The leaching and field pesticide residue calculations were made using Microsoft excel.

Results and Discussion

Percent recovery

Thiodicarb standard solutions in the range 0.1-1 ng/µl were added to inert soil, mixed in well manner and left overnight to ensure complete adsorption of the pesticide. Subsequently thiodicarb was extracted and run on HPLC. After calibration the observed percent recoveries of thiodicarb in soil were in range of 86.098-95.762%.

Limit of quantification and detection

LOQ and LOD for thiodicarb were determined at signal-to-noise ratio of 10 and 3, which were 0.005 mg/kg and 0.001 mg/kg respectively.

Influence of soil characteristics on adsorption and leaching of thiodicarb pesticide

Fate of pesticide in environment (soil, water and air), partitioning of pesticide among water and soil, their movement mechanisms such as volatilization, leaching and runoff all are controlled by adsorption. The destiny of pesticide is managed by three factors which are; properties of pesticide, soil characteristics and seasonal variations. Soil characteristics include texture, organic matter (OM), pH, cation exchange capacity (CEC) etc. Adsorption increases with increase in amount of OM, clay and CEC [18 - 21], while decreases with increase in value of pH [22, 23]. The soil used in our study had organic matter 0.89 % as shown in (Table 1), which was low as compared to reported in literature so adsorption should be lower. But soil texture indicates that the soil taken was sandy clay loam having 32.68 % clay which enhances adsorption of thiodicarb owing to greater surface area [24, 25]. The pH observed was 7.46, almost in neutral region so its affect on adsorption seems to be negligible. CEC recorded for soil was 24 meq/100g symbolizing the enhancement of adsorption. Overall the physicochemical properties observed in our experiment were low organic matter, high clay content, high CEC and neutral pH suggested moderate adsorption and low leaching of thiodicarb in selected soil.

***Table 1*. Physicochemical characteristics of soil.**

Parameter	Value
pH	7.46
Cation Exchange Capacity (meq/100g)	24
Organic Matter (%)	0.899
Total Organic Carbon (%)	0.522
Sand (%)	52.45
Slit (%)	14.87
Clay (%)	32.68
Classification	Sandy Clay Loam

Adsorption investigation

Movement of pesticide in soil was primarily controlled by kinetic adsorption [26]. The curve of kinetic sorption had revealed two areas shown in (Fig. 1), a quick adsorption happening at the start upto 7 hours and other was slow. After 10 hours equilibrium position was established and constant adsorption was seen. Due to physical affinity between the soil-thiodicarb and difference of concentration between pesticide solution and surface of soil, the fast adsorption was observed at initial [27].

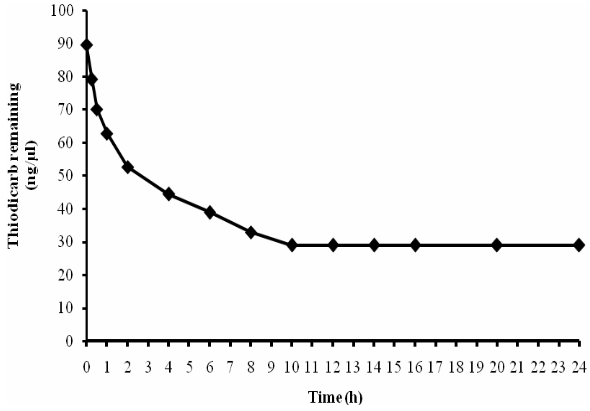

***Figure 1.* Kinetic adsorption of thiodicarb**

Both kinetic models pseudo first and pseudo second order were applied to view best fitted models, and it was evaluated that kinetic adsorption of thiodicarb followed pseudo first order with rate constant value of 0.711 h^{-1} as shown in Fig. 2 [28].

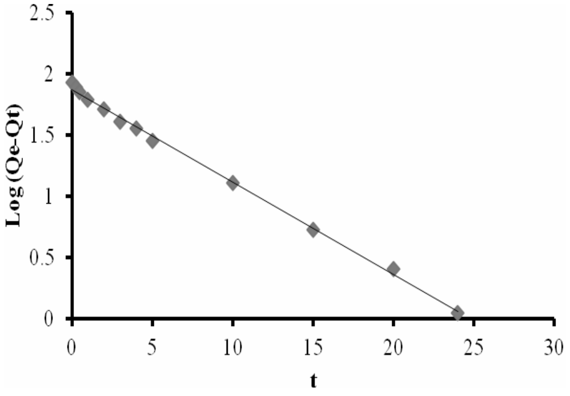

***Figure 2.* Pseudo first order plot for thiodicarb**

Equilibrium adsorption of thiodicarb was also examined using Langmuir and Freundlich isotherms and found that Freundlich model was followed by thiodicarb with multilayer adsorption capacity 3.749 mol/g and adsorption intensity 1.009 as shown in (Fig. 3) [29]. The partition coefficient normalized to organic matter (K_{OM}) calculated from Freundlich model was 417.018 L/kg, representing good adsorption power of thiodicarb.

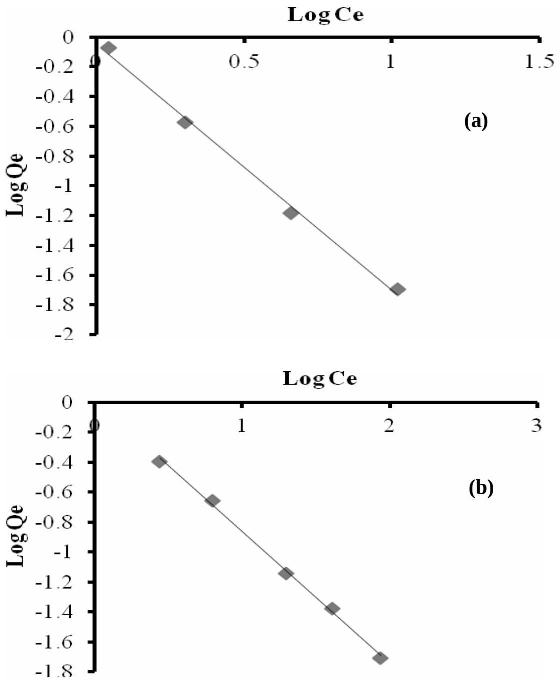

***Figure 3.* Freundlich isotherm for thiodicarb (a) at lower concentration (b) at higher concentration**

Leaching study

Column investigation of thiodicarb had revealed that this pesticide moves in water due to its solubility as well as remains adsorbed to soil as shown in (Table 2). Leaching with water decreases as time passes because in first portion of water its amount was higher than next [28, 30, 31]. In addition initially it was more available for water so forced easily as compared to coming parts. The leached amount of thiodicarb in first and last part of water was 1.075 and 0.003 ng/µl, same way adsorbed pesticide amount in first and last section of soil was 2.027 and 0.618 ng/µl.

***Table 2*. Adsorption and leaching of thiodicarb pesticide from column.**

Sample	Thiodicarb concentration found (ng/µl)
Water 01	1.075 ±0.13
Water 02	0.607 ±0.07
Water 03	0.319 ±0.12
Water 04	0.071 ±0.03
Water 05	0.003 ±0.02
Soil 0-10 cm	2.027 ±0.16
Soil 11-20 cm	1.084 ±0.27
Soil 21-30 cm	0.618 ±0.18

Field analysis

Field analysis indicated the non-leacher nature of thiodicarb because it remains adsorbed over upper layer of soil [32]. It has moved mainly up-to 20 cm soil depth; however minor amount was also seen in third sampling section from 21-30 cm. While not detected in fourth sampling part which starts from 31-60 cm soil deepness as given in (Table 3). The HPLC chromalogram of thiodicarb is shown in (Fig. 4), the retention time observed for thiodicarb was 2.530 in butter than reported studies [13-17]. Therefore only within three minutes the analysis can be finished, showing the simplicity and rapidity of developed method.

The soil used in column and taken from field has shown that thiodicarb was adsorbed on soil due to higher clay amount, improved CEC and almost neutral pH [22 - 25]. Generally, trend observed for adsorption was decrease as we go down in field soil from 5.079 to 0.009 ng/µl.

***Table 3*. Residue of thiodicarb found in field soil.**

Soil depth (cm)	Thiodicarb concentration (ng/µl)	Thiodicarb % in each layer
0-10	5.079 ±0.35	70.629
11-20	2.103 ±0.16	29.244
21-30	0.009 ±0.02	0.125
31-60	ND	-

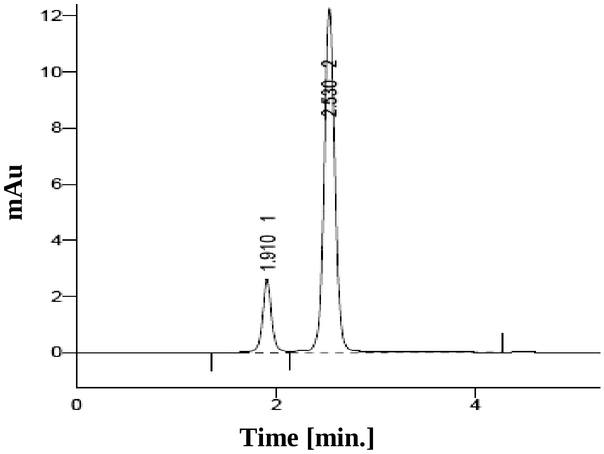

***Figure 4*. HPLC chromatogram of thiodicarb**

Conclusions

In current study the adsorption and leaching potential of thiodicarb were examined. Adsorption was divided in two sections kinetic and equilibrium. Experiment has revealed that thiodicarb has followed first order kinetic and equilibrium study shown that Freundlich model was best fitted. Therefore adsorption of thiodicarb was multilayer, reversible and non-ideal. Leaching study has proved intermediate mobility of thiodicarb with water due to its solubility, while field study shows the non-leacher nature. However both adsorption and leaching are heavily affected by soil characteristics. As the soil taken was sandy clay loam, due to clay texture adsorption was higher because of vacant sites existing and greater surface area. Due to this it remains adsorbed in above 20 cm soil layer as clearly seen from field study, minor amount was recorded in third layer of soil having 21-30 cm depth. Leaching poses risk to underground water and soil life while adsorption is reverse of this. Finally it was concluded that thiodicarb can be used in minor doses at the place of other highly toxic pesticides. But it should be remember that thiodicarb is also toxin killing insect means it will affect on our food chain, so avoiding use of pesticide is better practice if possible.

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