

STUDY OF ADSORPTION AND LEACHING BEHAVIOUR OF ZIRAM ON FOUR DIFFERENT SOILS

RAJINDER KASHYAP, ANIL THAKUR, H. K. THAKUR, D. K. SHARMA

Abstract: The use of pesticides has resulted in a serious environmental problem due to their leaching and migration to water sources. The objective of present work is to study the adsorption and leaching behaviour of ziram. To accomplish this, an extractive spectrophotometric methodology has been used which involves the reaction of ziram with copper (II) acetate in water to form isobutylmethylketone extractable yellow coloured complex showing maximum absorbance at 430nm. The soil-adsorption of the fungicide on four Indian soils of different soil characteristics has been studied by using a batch-equilibrium method and the various adsorption parameters viz. soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}), Gibb's free energy (ΔG°) and Groundwater Ubiquity Score (GUS) have been calculated. The leaching potential of ziram in terms of ground water ubiquity score (GUS) has been found below 1.8, which classify it as a nonleacher pesticide.

Keywords: Ziram, Copper (II) acetate, Soil adsorption, Ground water ubiquity score.

Introduction: Ziram, bis(dimethyldithiocarbamate)zinc, has been used as a broad spectrum dithiocarbamate fungicide and vulcanization and antioxidants additive in the rubber industry [1,2]. The fungicide has various adverse effects on non-target organisms including human being [2,3]. Applied pesticides will in one way or other end up in soil or water bodies. Soils and sediments are important sinks for pesticides because of their ability to sorb large amounts of these harmful compounds. Soil functions as chemical and biological filters that lessen the environmental impact of organic chemicals introduced into the environment by design or accident. Sorption of pesticides to the soil is one of the most important phenomena, which affect the pesticide transport, persistence, bioavailability and degradation [4]. Concern about the environmental impact of extensive use of pesticides has prompted research into the environmental fate of these chemicals. With a view to study the fate of ziram in soil and the extent of surface and ground water contamination, the soil-adsorption of the fungicide on four Indian soils of different soil characteristics has been studied by using a batch-equilibrium method. An extractive spectrophotometric methodology has been used which involves the reaction of ziram with copper (II) acetate in water to form isobutylmethylketone extractable yellow coloured complex showing maximum absorbance at 430nm. The Beer's law is obeyed up to $30.58 \mu\text{gml}^{-1}$. The various adsorption parameters viz. soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}), Gibb's free energy (ΔG°) and Groundwater Ubiquity Score (GUS) have been calculated.

Experimental Apparatus: Spectrophotometric measurements were made with a Varian-Cary 100 bio

UV-visible spectrophotometer. Incubator Shaker PT-422 was used in soil adsorption study.

Reagents and samples: Acetonitrile (Merck) was kept over phosphorus pentoxide (5 gL^{-1}) and distilled twice. The analytical standard of ziram (Fluka, Switzerland) was used and its stock solution (10^{-3}M) was prepared by dissolving 15.29 mg of ziram in acetonitrile and diluting to 50mL with the same solvent. Copper (II) acetate monohydrate (CDH, AR), its $\approx 0.01\text{M}$ solution in water was prepared by dissolving 0.2g of Copper (II) acetate in distilled water and diluting to 100mL with the same solvent. Isobutyl methyl ketone (MIBK, CDH, AR) was used as supplied.

Soil samples: The soils used in the adsorption study were collected from Solan District of Himachal Pradesh, India. The soils samples were air-dried, crushed with wooden mortar and sifted through 2mm sieve. Dried and sieved soil samples were placed in sealed glass jars and stored at room temperature.

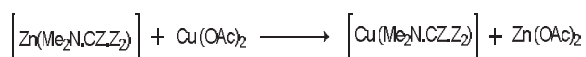
Buffer solution: The pH of buffer solution was optimised to ≈ 5.00 at which the extraction of the yellow coloured complex is maximum and this buffer was prepared by mixing 0.2M aqueous acetic acid and 0.2M aqueous sodium acetate in the ratio of 3:7 (v/v).

Preparation of calibration graph for pure compound: Aliquots (0.05-1.5mL) of the standard solution (10^{-3}M in acetonitrile) of ziram were taken in 100 mL-separating funnels and volume made to 2.0mL with the same solvent. Each solution was mixed with 5mL of water and 1mL aqueous copper(II) acetate ($\approx 0.01\text{M}$) and kept for 2 min. Each solution was then mixed with 5mL of buffer solution (pH ≈ 5.00). Each mixture solution was equilibrated two times with 4mL of MIBK for five minutes each. The yellow MIBK layer was separated and total volume made to 10mL with MIBK and dried over anhydrous

sodium sulphate (2g). The absorbance of yellow MIBK solution was measured at 430nm (Fig.1) against the reagent blank and a calibration graph was prepared. The relationship between concentration of ziram and absorbance was linear up to 30.5 $\mu\text{g mL}^{-1}$ (Fig.2).

Soil adsorption study: Ziram adsorption isotherm on four Indian soils of different soil characteristics (Table 1) were obtained by the batch equilibration technique using 50 ml conical flask. Triplicate soil samples (2g) were equilibrated with ziram solutions in the concentration range from 30.58-91.74 $\mu\text{g mL}^{-1}$ by shaking mechanically at room temperature ($25 \pm 1^\circ\text{C}$) for 24h equilibrium time. After equilibration, the suspensions were centrifuged and the equilibrium concentrations (C_e) were determined in supernatants by the method described above.

Results and discussion: The above method for the determination of ziram is simple, rapid and sensitive [ϵ , $1.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$]. Ziram in the range of 5-30 μg could be determined with a maximum relative standard deviation (RSD) of 0.9%. Of the various extracting solvents tested for extraction of the coloured product, MIBK is found to be the best for extraction because it extracts the complex quantitatively from aqueous solution ($\approx \text{pH } 5$) and the stability of the yellow colour is better (4hours). It may be mentioned that the coloured complex is also extractable in chloroform and other chlorinated hydrocarbons but the latter are found to be carcinogenic. The method has successfully been applied to the analysis of a commercial formulation of ziram for its active ingredient content for the purpose of quality control with recoveries of the active ingredient in the range of 98.4%- 99.1% of the nominal content with RSDs in the range of 0.64% to 0.90%. To assess the validity of the proposed method in soil adsorption study, effect of various common ions on the determination of fungicide was studied. The method was found to be free from interferences of most of common ions viz. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Pb^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} , NO_2^- , NO_3^- , SCN^- , PO_4^{3-} , CH_3COO^- generally present in soil.



Soil adsorption study: Adsorption isotherms have been evaluated by using Freundlich's adsorption equation :

$$X = K_f C_e^{n_f} \quad (1)$$

Where 'X' is the amount of pesticide adsorbed mg kg^{-1} of the adsorbent; ' C_e ' is the equilibrium solution concentration (mg L^{-1}); K_f and n_f are adsorption coefficients that characterize the adsorption capacity

of adsorbent and are calculated from the least square methods applied to the linear form of the Freundlich's adsorption equation:

$$\log X = \log K_f + n_f \log C_e \quad (2)$$

Other parameters for the adsorption process viz. distribution coefficient or soil-adsorption coefficient (K_d), Gibb's free energy (ΔG°), soil organic carbon partition coefficient (K_{oc}) and Groundwater Ubiquity Score (GUS) have been calculated by using equations 3-6 respectively [5-7].

$$K_d = \frac{X}{C_e} \quad (3)$$

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$K_{oc} = K_d \times \left(\frac{100}{\%O.C.} \right) \quad (5)$$

$$GUS = \log t_{1/2} \left[4 - \log(K_{oc}) \right] \quad (6)$$

Where R = gas constant, T = absolute temperature, $t_{1/2}$ = pesticide persistence (half life), OC = organic carbon content of soil. GUS score is used to study the leaching behaviour of pesticides and these can be classified as leacher ($GUS > 2.8$), transition ($2.8 > GUS < 1.8$) and non-leacher ($GUS < 1.8$) [8]. All these parameters for the adsorption of ziram on four Indian soils were calculated and the results are shown in Table 2.

The adsorption isotherms of ziram fungicide on four Indian soils were evaluated by Freundlich's adsorption equation and these isotherms may be classified as L-type of Gile's classification [9] (Fig. 3). L-types of isotherms represent a system where the solid surface has average affinity for the pesticide and the solvent is relatively inert. Freundlich's adsorption coefficients K_f and n_f were calculated from the plot of $\log X$ versus $\log C_e$ (Fig. 4) and results are presented in Table 2. The adsorption coefficient K_f represents the amount of pesticide adsorbed at an equilibrium concentration of img L^{-1} and n_f represents the variation in adsorption with varying concentration of pesticide [4]. The observed value of n_f was less than 1 in all four cases, indicating that with an increase in the concentration of pesticide, the percentage adsorption of the pesticide by the soil decreased. This might be due to the fact that at higher concentration, there is an increased difficulty to access the adsorption site [10].

Various adsorption parameters have been calculated and are presented in Table 2. The soil-adsorption coefficient (K_d) values for ziram are 6.04, 6.61, 7.62 and 7.78 for soil I, soil II, soil III and soil IV respectively. The value of K_d represents the extent of adsorption and in general higher the K_d value, the greater is the pesticide adsorption [4]. Hence, ziram is adsorbed maximally in the case of soil III and IV.

The soil organic carbon partition coefficient (K_{oc}) is less soil specific [11] and is calculated by normalizing adsorption coefficient (K_d) with the organic carbon (OC) content of the soil.

The adsorption of pesticide on soil depends on its characteristics and is affected by various parameters. The organic matter content of soils affects the adsorption of pesticide: higher the organic matter contents, higher the adsorption [12], this has been observed in soils III and IV. The cation exchange capacity (CEC) is another parameter that influences the adsorption of pesticide. The value of CEC is directly proportional to hydrophobic nature of adsorbent, i.e., greater the value of CEC of soil, its surface will be more hydrophobic. The organic pesticides being more hydrophobic (low water solubility) thus have higher adsorption affinity for the soils with higher CEC. The value of Gibb's free energy (ΔG°) for the adsorption of ziram was observed negative, suggesting the energetically favourable adsorption process. A number of models are available to evaluate the leaching potential of pesticide vis-a-vis-associated environmental pollution risk. Groundwater Ubiquity Score (GUS) is the most commonly used model which relates pesticide

persistence (half life) and adsorption in soil (K_{oc}). The leaching potential of fungicide in terms of GUS index was determined by using experimentally observed K_{oc} value for each soil sample and literature reported half life of ziram. The GUS for ziram has been observed below 1.8, which classifies it as a non-leacher pesticide. Therefore, the use of ziram fungicide does not represent the real hazard to ground water contamination.

Conclusion: The pesticide leaching is an important process with respect to contamination risk to aquatic environment. The values of soil organic carbon partition coefficient (K_{oc}) suggest moderate adsorption in soil types. Since ziram is moderately bound to soils, have low water solubility and short half life, so it is not expected to contaminate ground water. This is further supported by GUS values of ziram which are less than 1.8 for all the four soils used, classifying it as non-leacher pesticide. It is further concluded that the toxicity due to this fungicide can also be reduced by adjusting the application dose according to soil properties. The soils with high organic carbon content increase its adsorption and consequently reduce its leaching losses.

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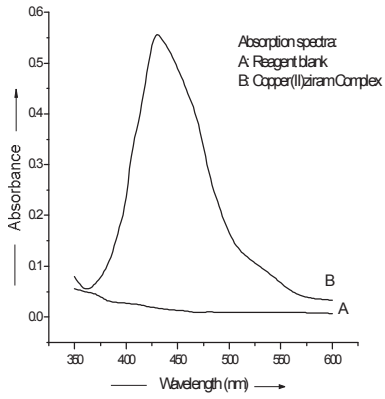


Fig 1. Absorption spectrum of Cu-ziram complex.

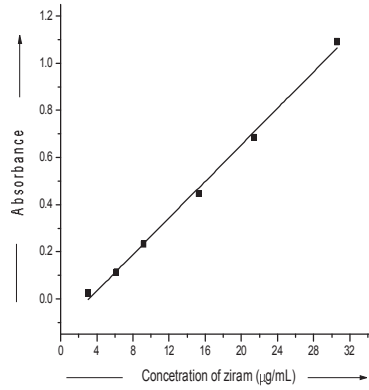
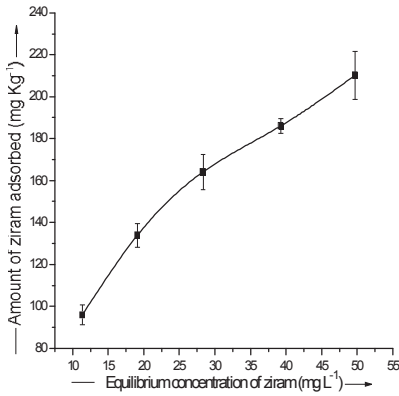
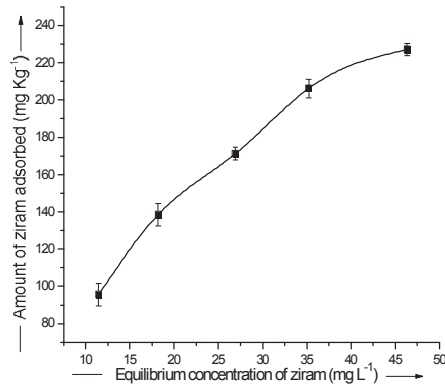


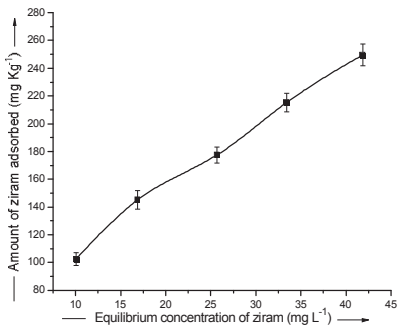
Fig 2. Relationship between absorbance and concentration (calibration graph) for ziram.



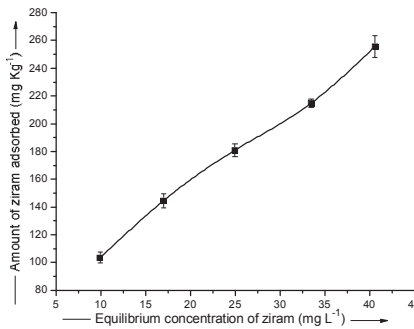
(a) Adsorption isotherm of ziram on soil I



(b) Adsorption isotherm of ziram on soil II



(c) Adsorption isotherm of ziram on soil III



(d) Adsorption isotherm of ziram on soil IV

Fig. 3. Adsorption isotherms of ziram (error bars represent the standard deviations of three replicates).

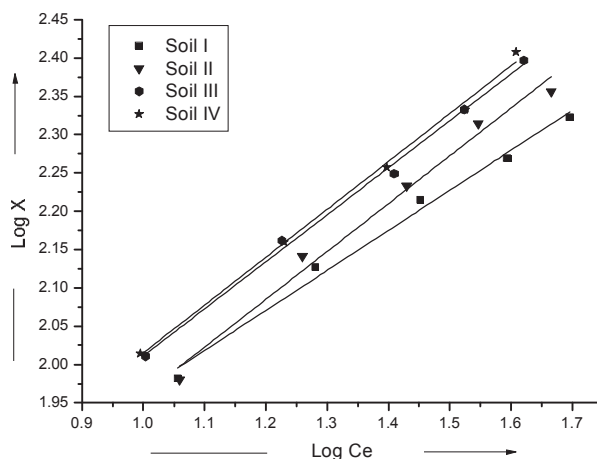


Fig. 4. Plot of log X versus log Ce for the evaluation of Freundlich's adsorption coefficients K_f and n_f for ziram

Soil Sample	Soil Texture	pH	Clay (%)	Organic carbon (%)	Cation Exchange Capacity (meq/100g)
I	Clay Loam	7.2	32.6	0.80	13.11
II	Silt loam	7.6	18.2	0.90	12.91
III	Sandy Loam	6.5	20.0	1.50	11.0
IV	Gravelly Sandy Loam	6.8	23.4	1.60	12.80

Soil	K_f	n_f	K_d	K_{oc}	Log K_{oc}	ΔG°	GUS
I	27.74	0.52	6.04	755	2.87	-4.456	0.90
II	21.68	0.62	6.61	734	2.86	-4.680	0.91
III	24.99	0.61	7.62	508	2.70	-5.031	1.04
IV	24.57	0.62	7.78	486	2.68	-5.085	1.06

Departments of Chemistry, Govt. P. G. College, Solan-173212, Himachal Pradesh, India.

rajumeena4@yahoo.in ; anil_t2001@yahoo.com

Department of Chemistry, Govt. College, Amb (Una), Himachal Pradesh, India.

harikrishan13@gmail.com

Department of Chemistry, Himachal Pradesh University, Shimla-171005, India.

dksharma_dk@rediffmail.com