SPECTRO PHOTOMETRIC METHODOLOGY FOR THE EVALUATION OF LEECHING BEHAVIOR OF BENOMYL ON TWO INDIAN SOILS

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ABSTRACT

An extractive Spectrophotometric method for benomyl adsorption in soils has been developed with a view of evaluate its leaching potential in terms of ground water ubiquity score (GUS). The method is based on the color reaction of n-butylamine (formed from the microwave assited alkaline hydrogen of the fungicide) with carbon disulphide and copper (II) chloride to form chloroform extractible yellowish copper(II) n-butyldithiocarbamate complex showing maximum absorbance at 380nm. The colour which develops immediately is stable for atleast 1h and fungicide can be determined in the range 4-72 μg mL^{-1} of benomyl solutions with maximum relative standard deviation of 1.5%. The adsorption isotherms on two Indian soils have been evaluated by Freundlich's adsorption equation. The GUS has been found before 1.8, classifying it as a nonleacher pesticide.

***Keywords: Benomyl, Microwave assisted hydrolysis, soil adsorption study.***

I. INTRODUCTION

Benomyl (methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate) is one of the important benzimidazolic systemic fungicides used to control a wide range of fungal diseases[1]. It has various adverse effects on non target organisms and has been classified as hazardous to human health[1-5]. Applied pesticides in one way or other end up in soil and subsequently to water bodies. Soil curtails mobility of pesticides chemicals by sorption and is a key process for deciding the ultimate fate of pesticide in terms of transport, persistence, bioactivity and consequently mobility and extent of surface and ground water contamination.

Various analytical methods developed for the analysis of benomyl viz. liquid chromatograph[7-8], HPLC[9,10], gas chromatography [11], spectroflourometry[7-8], HPLV[9,10], gas chromatography[11], spectroflourometry[12], flow injection[13] and densitometric,[14] are mostly based on its conversion to methyl 2-benzimidazole carbamate (MBC) commonly known as carbendazim or 2-aminobenzimidazole (2-AB) by acid/base hydrolysis. These methods require number of steps with strict adherence to experimental conditions during the hydrolysis of the fungicide, thus making the methods tedious and time consuming. A simple, sensitive and reliable extractive spectrophotometric method for the determination benomyl for studying its adsorption in soils to evaluate its leaching potential has been developed.

II. RESULTS AND DISCUSSION

The proposed method is based on the colour reaction of *n*-butylamine, one of the microwave assisted hydrolytic products of benomyl, with carbon disulphide and copper (I) chloride, to form a chloroform extractable yellowish copper (II) n- butyldithiocarbamate complex. That benomyl on hydrolysis forms MBC and *n*-butylamine and the later react with carbon disulphide and copper (I) to form yellow copper(I) dithiocarbamate are quite well known [15,16].

$$C_4H_9NH_2 + CS_2 + NaHCO_3 \longrightarrow C_4H_9NH.CS.SNa + H_2O + CO_2$$

$$2\ C_4H_9NH.CS.SNa + CuCl_2 \longrightarrow (C_4H_9NH.CS.S)_2Cu + 2NaCl$$
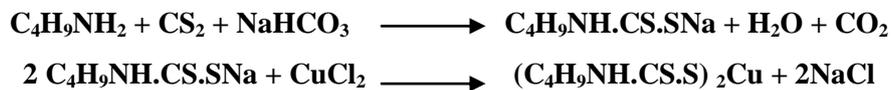
Under the optimized experimental conditions, the proposed extractive Spectrophotometric method obeys Beer's law in the range 4.0-$72.7\mu g\ mL^{-1}$ of benomyl solution. The molar absorptivity was found to be $2.0 \times 10^3\ L$. The adsorption isotherms of benomyl on two soils of different soil characteristics (Table1) were evaluated by Freundlich's adsorption eq.(1).

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

where X is the amount of pesticide adsorb $mg\ kg^{-1}$ of the adsorbent; C_e is the equilibrium in

Table 1. Characteristics of the different Indian soils used in the adsorption study of benomyl

Soil Sample	pH	Clay (%)	Organic carbon (%)	Cation Exchange Capacity (meq/100 g)
I	6.5	20.0	1.5	11.0
II	6.8	23.4	1.6	12.8

concentration in solution $(mg\ L^{-1})$; K_f and n_f are adsorption coefficients which are calculated from the least square methods applied to the linear form of the Freundlich's adsorption eq.(2) by the plot of log X versus log C_e(Fig.1).

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

The various adsorption parameters viz. soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}), Gibb's free energy (ΔG^o) and groundwater ubiquity score (GUS) have been calculated by using eqs.[3-6] respectively [17-19] and are given in Table 2.
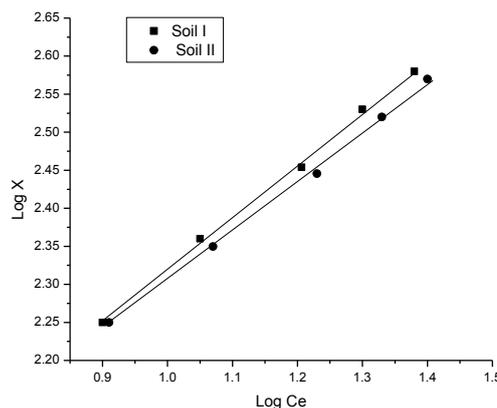
Table 2. Adsorption parameters for the adsorption of benomyl fungicide on four Indian soils

Soil	k_f	n_f	k_d	k_{OC}	ΔG^o	GUS
I	43.65	0.661	17.86	2232	-7.142	0.31
II	42.22	0.699	19.02	2113	-7.298	0.32

$$Kd = \frac{X}{C_e} \qquad (3)$$

$$\Delta G^o = -RT \ln K_d \qquad (4)$$

$$K_{oc} = K_d \times \left[\frac{100}{\%OC} \right] \qquad (5)$$

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

where R=gas constant, T=absolute temperature, $t_{1/2}$ = pesticide persistence (half life), OC =organic carbon content of soil therms obtained for benomyl are almost L-type[20] representing a relatively high affinity between the solid surface and solute which is further supported by value of $n_f < 1$ (Table2) Higher values of K_f also favour the adsorption phenomena and consequently lower the tendency of pesticide to move in soil. The organic matter content and the clay content of soils also play a very important role in the sorption of pesticides as these components provide soils with an increased number of adsorptive sites onto which pesticides molecules can bind[21]. Cation Exchange Capacity (CEC) which is directly proportional to hydrophobic nature of adsorbent also affects the adsorption process. Benomyl being more hydrophobic exhibit higher adsorption affinity for the soils with higher CEC. The higher K_d values of benomyl with both soil types further substantiates the greater benomyl adsorption. The high values of K_{OC} also suggest that benomyl is strongly adsorbed to soils. The leaching potential of fungicide was evaluated in terms of GUS index to be (0.31-0.32) are below 1.8, which classifies it as a non-leacher pesticide[23] which has been found by using experimentally observed K_{OC} value for each soil sample and literature reported half life of benomyl[3].

III. EXPERIMENTAL

3.1 Reagents and equipments

Acetonitrile (Merck, AR) was kept over phosphorus pentoxide (5 g L^{-1}) and distilled twice. The analytical standard of benomyl (Sigma-Aldrich Labochemikalien GmbH, Germany) was used and its stock solution (10^{-3} mol L^{-1}) was prepared in acetonitrile. Copper (II) chloride and its standard solution (0.01 mol L^{-1}) in water was prepared by dissolving a little more than the calculated amount of the compound in water and standardized iodometrically[24]. A 2% solution of carbon disulphide (Merck, AR) in acetonitrile was used. Sodium bicarbonate (CDH, LR), 0.1 mol L^{-1} aqueous solution was used. The soils used in the adsorption study were collected from Solan, region of Himachal Pradesh, India.

All the Spectrophotometric measurements were made with a Spectronic $20D^+$ spectrophotometer with 1 cm matched glass cells. Domestic microwave oven, Samsung was used for microwave assisted hydrolysis.

3.2 Preparation of calibration graph for pure compound

Aliquots (0.1-2.0 mL) of standard solution of benomyl (10^{-3} mol L^{-1} in acetonitrile) were taken in 10 mL measuring flasks and volume made to 2.0 mL with acetonitrile. Each solution was mixed with 1 mL aqueous sodium bicarbonate (0.1 mol L^{-1}) solution, 0.5 mL of 2% carbon disulphide (in acetonitrile) and 1.5 mL of distilled water and kept in the microwave oven for 40 s and allowed to stand for 5 min. The hydrolyzed benomyl solution was then mixed with copper (II) chloride (1 mL, 0.01 mol L^{-1}). Each mixture solution was equilibrated twice with 4mL of chloroform for five minutes. The chloroform layer was separated, volume made to 10 mL with chloroform and dried over anhydrous sodium sulphate (1.5 g) and the absorbance measured at 360nm against a reagent blank and a calibration graph was prepared (Fig.2).
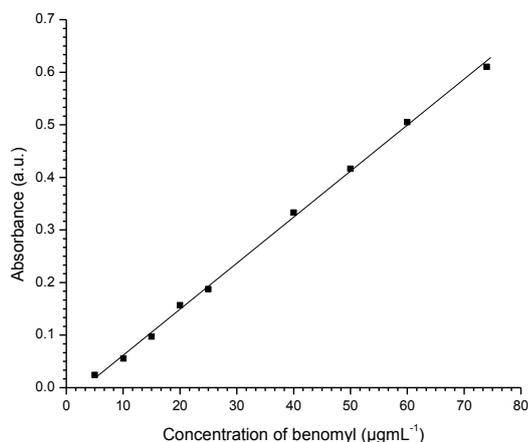
3.3 Soil adsorption study

Benomyl adsorption isotherms on four Indian soils of different soil characteristics (table1) were obtained by the batch equilibration technique using 50 mL conical flask. Triplicate soil samples (2.0 g) were equilibrated with aqueous-acetonitrile benomyl solutions in the concentration range from 43.5-101.6µg mL^{-1} by shaking in Incubator Shaker for 12 h equilibrium time. After equilibration, the suspensions were centrifuged and the equilibrium concentrations (C_e) were determined in supernatants by the Spectrophotometric procedure described above.

IV. CONCLUSION

The proposed method for the determination of benomyl is simple, rapid and reliable and is of wide applicability. Adsorption studies of benomyl indicate that it is strongly adsorbed on to soils and this consequently inhibits its penetration into water sources. This is further supported by groundwater ubiquity score (GUS) which is below 1.8, classifying it as a non-leacher pesticide and hence it does not represent hazard to ground water contamination.

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