https://doi.org/10.29321/MAJ.10.A02338

Madras Agric. J. 72 (1): 16—21 January 1985

ADSORPTION OF CARBENDAZIM (MBC) BY SOILS AND CLAY MINERALS*

S. G. Patil and P. B. Deshpande

The effect of temperature, clay type, organic matter, pH and soil types of adsorption of carbendazim was investigated. Adsorption of carbendazim decreased with increase in temperature on both Ca-Montmorillonite and Ca-Kaolinite clays. Among clay types, Ca-montmorillonite was superior in adsorbing this fungicide over Ca-Kaolinite. The adsorption of carbendazim was inferred to be through physical means under the specified conditions from the values of change in free energies. Adsorption was found to be highest on activated soils as reflected by their higher values of Freundlich's constants followed by natural and organic matter-free soils, respectively. The decreased adsorption of carbendazim on removing organic matter with H_2O_2 pretreatment suggested the importance of organic matter in adsorption The effect of pH on adsorption of this fungicide revealed ionization of molecules through protonation at lower pH values. Thus carbendazim was adsorbed on soils in larger quantities as a result of protonation followed by ion-exchange process. Among soils, highest adsorption of this fungicide was found in laterite soils.

Carbendazim (Methyl-2-benzimidazole carbamate) is a broad spectrum systemic fungicide used extensively to control fungal diseases. It is a moderately weak base (pka 4.48) and strongly adsorbed by soils as protonated species (Aharonson and Kaf Kafi, 1975). Previous reports have shown that uptake of systemic benzimidazoles by plants from soil is very inefficient due to its strong adsorption on soils. It has been also reported that uptake of benomyl by crops was more in sandy soils than from clay soils. However, an increased uptake of the fungicide was observed in soils with low in organic matter and relatively higher pH (Austin and Brigg's, 1976). From the earlier reports it is clear that the effectiveness of fungicide is decided on the extent of adsorption into the adsorbent surfaces. Therefore, a great deal of investigations are needed to understand the adsorption behaviour of this fungicide. Literature on this aspect is still lacking and needs to be studied further.

The present work envisages the studies on adsorption and describes adsorption as a function of some physico-chemical properties of soils.

MATERIALS AND METHODS

The technical grade (98 per cent pure) of carbendazim was obtained from M/s. BASF India Limited, Bom-

Part of the ph. D. thesis submitted by Senior author to the University of Agricultural Sciences, Bangalore.

Department of Soils Science, University of Agril. Sciences, Bangalore-24

bay. All solvents used for extraction of carbendazim were of analytical grade. Pure clay minerals were obtained from Wands Natural Scienees establishment Inc. U.S.A. Tha soil samples used for adsorption studies represented Red Sandy loam from Bangalore, Sandy clay loam from Coorg and clay soil from Dharwad. The physico-chemical characteristics of the soils are presented in Table 1.

ADSORPTION EXPERIMENTS

1. Effect of temperature and clay type on adsorption

Effect of temperature and clay type was carried out on homoionic clays i.e., clays saturated with Ca. One hundred miligrams of clays were dispensed into 50ml glass centrifuge tubes, to which 20ml of 0.002 *M* $CaCl_2$ having graded amounts (ranging from 100-500/ug/g) of carbendazim were added. The clay suspensions were allowed to equilibrate in incubator at 18$\pm$ 1° C, 25$\pm$ 1 °C and 37$\pm$1°C for 8 hours. At the end of the incubation period, the suspension were shaken for 2 hrs and centrifuged at 2000 rpm for 5 min The centrifugate was used in the extraction of carbendazim

2. Effect of organic matter on adsorption

The investigation on the effect of organic matter on adsorption was carried out on a) activated soil (soils were heated at 108°C for 6 hrs). b) Organic matter-free soils (soils were oxidised with H_2O_2 to remove organic matter) c) natural soil (used as it is).

To 2 g each soil, 20ml of 0.002 *M* $CaCl_2$ solution containing graded amounts of carbendazim (ranging from 5-30/ug/g) were transferred to equilibrate for 2 hours through shaking the soil suspension, after shaking they were centrifuged at 2000 r.p.m. for 5 min. and centrifugate was extracted for the fungicide.

3. Effect of pH on adsorption

Adsorption of carbendazim as a function of pH was studied by adjusting the pH of soil suspension with dil. HCl or NaOH to 5.0, 7.0 and 8.6 values. The equilibriation and other details remained same as mentioned under Para II above.

Fungfcide analysis

Aliquots of the supernatant remained after centrifugation in different experiments were extracted for recodering carbendazim. The extraction and clean up procedures followed remained same as described by Austin and Brigg's (1976). Carbendazim extracted by above procedure was assayed in Beckman Spectro-photometer (UV/visible) Model 24 at 282 nm using 0.1 *N* HCl as reference sample. The data obtained on quantities of carbedazim remaining in equil. solution and the quantity adsorbed were transformed into log from to conform with an empirical Freundlich's equation to find out k and n values to describe adsorption behaviour of carbendazim in soils.

TABLE 1 Properties of the soils used in the study

Soil	Textural class	Size fraction per cent of total			pH (1:2.5 Soil-Water Suspension)	CEC me 100g	Org. carbon (percent)	Specific surface area m^2/g
		Sand	Silt	Clay				
Red (Rhodustalf)	Sandy loam	75.5	9.5	14.8	6.6	14.2	0.51	28.5
Laterite (Haplustox)	Sandy clay loam	53.6	11.6	27.6	5.8	21.3	0.60	36.3
Black (Grumaquert)	Clay	15.2	13.9	56.6	8.1	69.9	0.46	763.3

TABLE 2. Adsorption of carbendazein by clays at different temperature.

Adsorbent	18±1°C			25±1°C			37±1°C		
	k	n	ΔG K-Cal Mole^{-1}	k	n	ΔG K-Cal mole^{-1}	k	n	ΔG K-Cal mole^{-1}
Ca-Montmorillonite	33 50	2.40	−2.09	25.12	2.17	−1.92	16.79	1.94	−1.69
Ca-Kaolinite	23.71	1.86	−1.88	12.59	1.50	−1.51	9.44	1.49	−1.34

TABLE 3 Relationship of pH and organic matter with Freundlichs constants for the adsortion of carbendazein by soils

Soil type	Organic matter						pH					
	Activated		Natural		Organic matter-free		5.0		7.0		8.6	
	k	n	k	n	k	n	k	n	k	n	k	n
Black	5.50	1.57	4.17	1.43	1.15	0.91	5.74	1.38	2.63	1.29	1.66	1.07
Red	1.59	1.00	1.20	0.99	1.10	1.04	3.02	1.11	2.29	1.06	1.26	1.14
Laterite	3.80	1.67	2.90	1.50	1.20	1.25	6.03	1.43	4.57	1.29	2.51	1.05

RESULTS AND DISCUSSION

i. Effect of temperature and clay type on adsorption

The values of k and n obtained are given in Table 2. Adsorption of carbendazim decreased as equilibration temperature increased indicated by the decrease in the values of both k and n. Among clay tppes, Ca-Montmorillonite adsorbed larger amounts of this fungicide compared to Ca-Kaolinite. As the adsorption is extermic, the increase in equilibration temperature resulted in a significant decrease in adsorption (Fig. 1). The results in respect of Freundlichs constant showed an inverse relationship

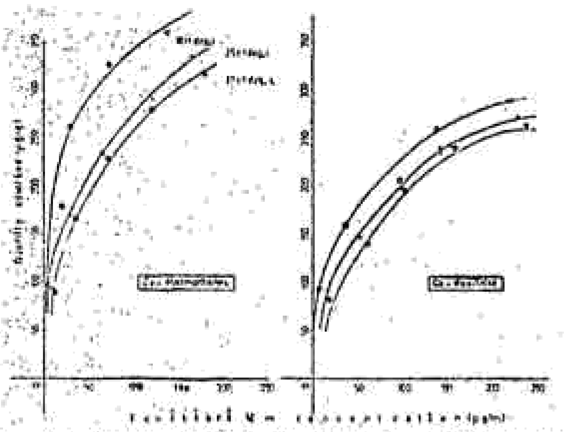

FIG. 1 ADSORPTION ISOTHERMS OF CARBENDAZIM FOR CLAYS AT DIFFERENT TEMPERATURES

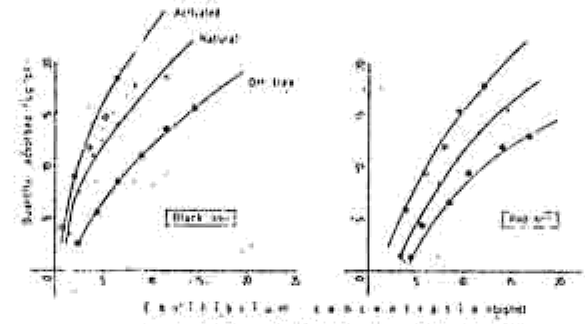

FIG. 2 ADSORPTION ISOTHERMS OF CARBENDAZIM FOR SOILS

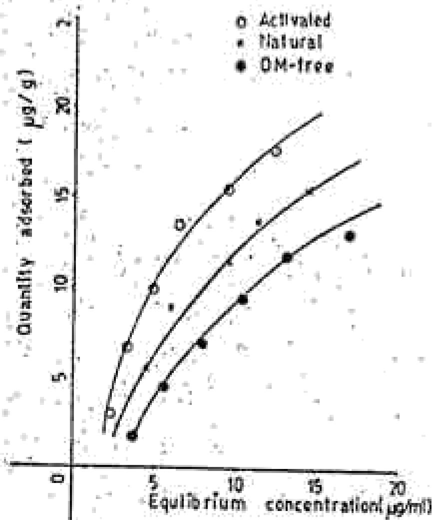

FIG. 3 ADSORPTION ISOTHERMS OF CARBENDAZIM FOR LATERITE SOIL

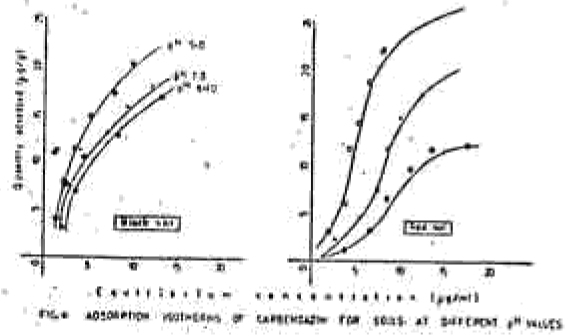

FIG. 4 ADSORPTION ISOTHERMS OF CARBENDAZIM FOR SOILS AT DIFFERENT pH VALUES

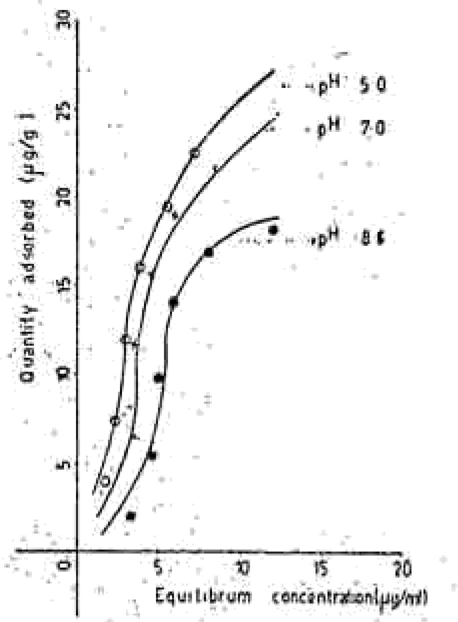

FIG. 5 ADSORPTION ISOTHERMS OF CARBENDAZIM FOR LATERITE SOIL AT DIFFERENT pH VALUES

with temperature. The decrease in adsorption with temperature is expected due to the increased tendencies of the biocide molecule to escape from the surface and increased solubility (Bailey and White, 1970; Mithyantha, 1973 and Kausalya *et al.*, 1982). The velues of standard free energy change were negative suggesting the spontenity of the adsorption reaction. As the values of ΔG observed were relatively lower than the values reported for chemisorption (Hamakar and Thomson, 1972) the adsorption of this fungicide on both clay types appeared to be mainly through physical forces under these experimental conditions.

ii. Effect of organic matter on adsorption

Results on adsorption of carbendazim in terms of k and n showing the effect of organic matter are presented in Table 3. Adsorption of carbendazim was highest in all activated soils, (as values of k remained highest) and lowest in organic matter free soils (Fig. 2, 3). It can be reasoned that on activation of soils, water and air covering active surfaces of the adsorbent are removed and it thereby facilitates greater adsorption of biocide molecules. However, adsorption remained intermediate in case of natural soil. In general, it was noticed that on destruction of organic matter from soils with Hydrogen peroxide pre-treatment, there was reduction in adsorption of carbendazim. The magnitude of reduction on an average ranged from 15-30 per cent. From the foregoing discussion it is clear that organic matter plays an important role in adsorption of this fungicide. Similar observations on the importance of organic matter in adsorption of carbendazim were reported by Austin and Brigg's(1976), Wahid and Sethunathan (1978) and Felsot and Dahm (1979).

iii. Effect of pH on adsorption

The results presented in Table 3 illustrates the change in the extent of adsorption in terms of Freundlich's constants with pH. Over the range studied, adsorption decreased as pH increased (Fig. 4, 5). Adsorption of carbendazim remained highest in case of laterite soil followed by black and red soils, respectively. The higher adsorption of carbendazim by laterite soils could be attributed to its low pH and relatively higher organic matter status. In general, it was observed that adsorption was found to be highest in all soils when pH was maintained at a value of 5.0 and decreased as the pH value increased to 8.6. The magnitude of adsorption of this fungicide diminished significantly with increase in pH of soil suspension. The higher adsorption at low pH conditions is possible due to protonation of the molecules as well as formation of complexes with hydrated-Al present under low soil pH conditions. Similar observation on the formation of coordinated complexes with metal ions has been reported for triazines by Hance (1969).

As reported earlier by Ahoronson and Kafkafi (1975), the higher adsorption of carbendazim in low pH condition is explainad on the basis of protonation of these molecules and thereby adsorbed on to surfaces of soil through ion-exchange processes. The results in this investigation are in conformity with earlier findings of the above workers. Adsorption of carbendazim is found to be pH dependent and its higher adsorption in acidic environment could be through protonation as shown under.

(Protonated species)

Thus, in the presence of higher hydrogen ion activity, carbendazim becomes protonated at the heterocyclic-N atom. The protonateb species becomes strongly adsorbed and in greater amounts on to the surfaces of the adsorbents.

REFERENCES

AHARONSON, N. and U. KAFKAFI, 1975. Adsorption, Mobility and persistence of thiabendazole and methyl-2-benzimidazole carbamate in soils. *J. agric.* Fd. Chem., *23*: 720-724.

AUSTIN, D. J. and G. G. BRIGG'S, 1976. A new extraction method for benomyl residues in soil and its application in movement and persistence studies. Pestic. *Sci.* *7*: 201-210

BAILEY, G. W. and J. L. WHITE, 1970. Factors influencing the adsorption desorption and movement of pesticides in soils. Residue Rev. *32*: 28-92

FELSOT, A. and P. A. DAHM, 1979. Sorption of organophosphorus and carbamate insecticides by soil. *J. agric.* Fd. Chem. *27*: 557-563.

HAMAKAR, J. W. and J. M. THOMSON, 1972. Adsorption. In: Organic chemicals in the soil environment (Eds. Goring, C. A. I. and Hamakar, J. W). Marcel Dekkar Inc. New York.

HANCE, R. J., 1969. Influence of pH, Exch. cation and the presence of Organic matter on the adsorption of some herbicides by montmorillonite. *Can. J. So il Sci.* *49*: 357-364.

KAUSALYA, T., RAMAN, S. and K. V. RAMAN 1982. Adsorption of terbutryne on metal-montmorillonites. *J. Indian Soil Sci.*, *30*: 13-21.

MITHYANTHA, M. S. 1973. Studies on the retention and persistence of pesticides in soils. Ph. D. thesis submitted to the University of *Agril. Sciences*, Bangalore.

WAHID, P. A. and N. SETHUNATHAN, 1978. Sorption-Desorption of parathion in soils. *J. agric.* Fd. Chem., *26*; 101-105.