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Sorption of Pendimethalin on Soils of Andhra Pradesh

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ABSTRACT

Adsorption desorption of pendimethalin in soils was studied by Batch equilibrium technique at five different initial concentrations of pendimethalin. Adsorption isotherms were conformed to the Freundlich equation. The desorption process exhibited pronounced hysteresis in all the soils, which was more prominent when desorption was carried out at higher concentration of herbicide and the percent cumulative desorption was high in soils with low organic carbon content .The values of Freundlich constant, K_f were ranged from 0.28 to 2.83 for pendimethalin, The Freundlich constants K_f and n increased with increasing initial concentration of adsorbed herbicide thus confirming the irreversible nature of the adsorption of pendimethalin of these soils. The per cent cumulative desorption was high in soils with low organic carbon content. Freundlich 'K_f' values which indicate the extent of binding of herbicide to the soil constituents were positively and significantly correlated with organic carbon (r = 0.94**), clay content (r = 0.91**) and clay + OC (r = 0.92**).

Key words : Freundlich Constants, Hysteresis, Pendimethalin, Sorption.

Pendimethalin(N-(1-ethylpropyl)–3,4-dimethyl-2,6-dinitrobenzenamine) belongs to dinitroaniline group used as pre-plant or pre emergence application for control of most of the annual grasses and broad leaved weeds. When a herbicide is applied to soil, it undergoes a number of process which determine its fate in soil. Adsorption – desorption is an important process for determining the ultimate fate of herbicides in soil because detoxification mechanisms such as degradation, metabolism, microbial uptake and mobilization are operative only on the non-sorbed fractions of the chemical to the sites on soil mineral or organic surfaces. Adsorption –desorption influences mobility, persistence, degradation and volatility of pesticide in soil.(Kalpana *et al.*,2002). Adsorption decreases the concentration of chemical in solution and decrease bioavailability. Desorption of herbicide is also critical in determining the herbicide available to the target species or the loss of herbicide through runoff and percolation which causes ground water pollution. Therefore present investigation was to study the adsorption- desorption of pendimethalin on four soil types of AndhraPradesh.

MATERIAL AND METHODS

Soil samples were collected from different Agro climatic zones of Andhra Pradesh and at each selected location, the soil samples were collected from 15-20 different spots at a depth of 0-22 cm, quartered and about 5 to 10 kg of each soil sample was brought to the laboratory, air dried under shade and sieved through a 2mm size sieve. These 2 mm sieved soils were properly labeled and stored in cloth bags for further studies.

Soil pH was determined in 1: 2.5 soil : water suspension by stirring up to 30 minutes using a Digisun digital pH meter (DI-707) with combined electrode assembly. The total soluble salt content was estimated by determining the electrical conductivity in 1:2 soil water extract (after stirring for half an hour) using EC bridge (DI-909) and was expressed as dS m^{-1} (Jackson , 1973). The organic carbon content was determined by wet digestion method of Walkley and Black (1934) as described by Jackson (1973) and expressed in g kg^{-1}.

Cation exchange capacity of soils was determined as per the method as suggested by Richards *et al.*(1954) using sodium acetate, ethanol and ammonium acetate and CEC of soils was expressed as c mol (p+) kg^{-1} soil. Mechanical composition of soils was determined by the International pipette method (Piper,1950). The relative proportions of sand, silt and clay of soils were determined to decide their textural class by using textural triangle. The physic chemical properties of soils were given in Table1.

Table 1. Physico-chemical characteristics of soils under study.

Soil	pH	EC (dS/m)	OC (g/kg)	Sand	Silt	Clay	Texture
S1	7.82	0.22	8.5	55.8	11.0	33.2	Clay loam
S2	8.65	0.29	4.5	84.4	2.0	13.6	Loamy sand
S3	7.71	0.24	3.1	74.40	13.00	12.60	Sandy loam
S4	6.57	0.16	5.3	76.00	0.60	23.40	Sandy clay loam

Technical grade pendimethalin (94.5 % purity) obtained from M/S BASF India Ltd., was used in the present investigation. Spectra of pendimethalin solution (10 µg mL^{-1}) were scanned in UV range to determine the wave length of maximum absorbance on a UV Visible spectrophotometer (GS 5701) using matched silica cuvettes. Pendimethalin showed maximum absorbance in visible range at 420 nm of and it was used as ë max for further studies.

Adsorption-desorption was conducted by equilibrating five grams of soils (2 mm) and treated with initial pendimethalin concentrations of 0,10,20,30,40 and 50 ìg mL^{-1} in 1 X 10^{-2} M $CaCl_2$ solution and incubated for 24 hrs at 27$\pm$1°C . The soil suspension was later centrifuged at 5000 rpm for five minutes and five mL of supernatant was taken out and absorbance of pendimethalin was measured at 420 nm. To the remaining slurry containing 15 mL solutions of pendimethalin solution and soil, 5 mL of $CaCl_2$ solution (1 X 10^{-2} M) was added to make solution to 20 ml and again incubated for 24 hrs and centrifuged at 5000 rpm for five minutes to determine the equilibrium concentration.

This process was repeated for 5 consecutive days. Identical soil blanks were also maintained simultaneously and the net absorbance of equilibrium concentration at each stage was obtained by subtracting the absorbance of blanks. The adsorption - desorption experiment was carried out in quadruplicates.

The amount of herbicide desorbed was calculated as follows:

Con = Cen-1 x 15/20 ;Where, Con= initial concentration of pendimethalin on n^{th} day;

Ce n-1 = equilibrium concentration on (n-1)th day;

Amount desorbed on nth day is given by (Cen– Con) x 20

The data on adsorption was analyzed by using Freundlich equation and the Freundlich constants were calculated.

Freundlich adsorption equation

The equation may be expressed as,

$x/m = K_f C^{1/n}$

x/m = amount adsorbed per unit mass of adsorbent ;

C = equilibrium concentration

K_f= Freundlich constant related to the strength of binding;

n= Constant which is less than 1

The constant K_f is related to strength of binding and depends on temperature.

K_f and n are determined from a logarithmic transformation of the equation, which is linear, $\text{Log } x/m = \log K_f + 1/n \log C$

The constant K and n were determined from the plot of log x/m vs. log C, the intercept and slope being log K and l/n, respectively.

RESULTS AND DISCUSSION

The adsorption isotherms of pendimethalin were found to be parabolic in nature with an initial 'S' shaped curve. S shaped isotherm indicates a stronger initial competition of water molecules to the adsorbent as compared to the herbicide, thereby indicating the initial resistance to the adsorption of herbicides to be overcome later by the co-operative effect of the adsorbed molecule.(Aravind *et al.,*2000).

The desorption isotherms did not coincide with adsorption isotherms. Desorption of both herbicides from soils indicated that slope of desorption isotherms was much lower than the slope of adsorption isotherms and less amount of herbicide was present in equilibrium solution than

Table 2 . Desorption of adsorbed pendimethalin from Alfisol (S1).

I.C	I Day		II Day			III Day			IV Day			V Day			% C.D	% C.A
	E.C	A.A	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D		
10	9.65	1.42	7.24	1.01	0.41	5.43	0.71	0.30	4.07	0.53	0.18	3.05	0.44	0.09	69.0	30.0
20	18.78	4.90	14.09	3.95	0.95	10.56	3.24	0.71	7.92	2.68	0.56	5.94	2.26	0.42	53.8	46.2
30	27.49	10.05	20.62	8.59	1.46	15.46	7.41	1.18	11.60	6.47	0.94	8.70	5.86	0.61	41.6	58.4
40	36.49	14.04	27.37	12.21	1.83	20.53	10.57	1.64	15.39	9.29	1.28	11.55	8.36	0.93	40.4	59.5
50	46.11	15.55	34.58	13.69	1.86	25.94	12.03	1.66	19.45	10.72	1.31	14.59	9.77	0.95	37.1	62.9

Table 3. Desorption of adsorbed pendimethalin from Alfisol (S2).

I.C	I Day		II Day			III Day			IV Day			V Day			% C.D	% C.A
	E.C	A.A	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D		
10	9.54	3.95	7.16	3.12	0.63	5.37	2.40	0.72	4.02	1.96	0.44	3.02	1.61	0.35	41.5	58.5
20	18.37	9.70	13.78	8.45	1.25	10.33	7.36	1.09	7.75	6.53	0.83	5.81	5.88	0.65	39.3	60.7
30	26.04	15.95	19.61	14.02	1.93	14.70	12.89	1.13	11.03	11.93	0.96	8.27	11.19	0.74	29.8	70.2
40	34.60	21.60	25.95	19.28	2.32	19.46	17.64	1.61	14.60	16.25	1.42	10.95	15.44	0.81	28.5	71.5
50	44.19	23.25	33.14	20.84	2.42	24.86	19.08	1.76	18.64	17.47	1.61	13.98	16.61	0.86	28.5	71.5

during adsorption. The desorption processes exhibited and the isotherms showed consistent hysteresis during desorption (Amit *et al.*, 2005; Nagamadhuri, 2003; Kalpara *et al.*, 2002; Arvind *et al.*, 2000; Jenks *et al.*, 1998; Prakash and Suseela Devi, 1998; Mersie and Sey bold,1996). The percent cumulative desorption of pendimethalin varied from 36.8 % to 69.0% for 10 µg mL^{-1},from 29.7% to 53.8 % for 20 µg mL^{-1} from 21.9 % to 41.6 % for 30 µg mL^{-1}, from 21.2 % to 40.40 % for 40 µg mL^{-1} and from 19.0 % to 37.1 % for 50 µg mL^{-1} .

The desorption of pendimethalin in selected four soils varied in the order: $S_3 > S_2 > S_4 > S_1$.

The higher adsorption on S_1 may be due to high organic carbon and clay content. Freundlich 'K_f' values which indicate the extent of binding of herbicide to the soil constituents were positively and significantly correlated with organic carbon (r = 0.94**), clay content (r = 0.91**) and clay + OC (r = 0.92**). Organic carbon content has been shown to be the first critical parameter positively and significantly correlated with adsorption of pendimethalin in soils (Johnson and Sims, 1993; Moreau and Mouvet, 1997).Clay content of soil is said to be another critical parameter in adsorption of pendimethalin in soils and its role is often masked by that of organic matter and this can become a significant factor when organic carbon content decreases

As the initial concentration increased there was a gradual decrease in desorption. Aravind *et al.* (2000) reported that the percent desorption of pendimethalin was varied from 29.06 to 40.1 in different soils . The adsorption-desorption isotherms were

Table 4. Desorption of adsorbed pendimethalin from Vertisol (S3).

I.C	I Day		II Day			III Day			IV Day			V Day			% C.D	% C.A
	E.C	A.A	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D		
10	8.66	4.58	6.64	3.90	0.68	4.98	3.44	0.46	3.74	3.13	0.31	2.80	2.89	0.24	36.8	63.2
20	17.32	10.72	12.99	9.60	1.12	9.74	8.74	0.86	7.31	8.11	0.63	5.48	7.53	0.58	29.7	70.3
30	25.54	17.85	19.15	16.49	1.36	14.36	15.44	1.05	10.77	14.58	0.86	8.08	13.94	0.64	21.9	78.1
40	33.85	24.60	25.39	23.02	1.58	19.04	21.66	1.36	14.28	20.45	1.21	10.71	19.37	1.08	21.2	78.8
50	42.94	28.25	32.20	26.64	1.61	24.15	25.24	1.40	18.11	23.98	1.26	13.59	22.87	1.11	19.0	81.0

Table 5. Desorption of adsorbed pendimethalin from Vertisol (S4).

I.C	I Day		II Day			III Day			IV Day			V Day			% C.D	% C.A
	E.C	A.A	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D	E.C	A.A	A.D		
10	9.83	1.56	7.37	1.32	0.24	5.53	1.11	0.21	4.15	0.98	0.13	3.11	0.86	0.12	44.8	55.2
20	19.48	8.44	14.61	7.06	1.38	10.96	6.05	1.01	8.22	5.25	0.80	6.16	4.85	0.40	42.3	57.7
30	28.61	14.55	21.46	12.55	2.00	16.09	11.12	1.43	12.07	9.85	1.27	9.05	8.95	0.90	38.5	61.5
40	36.85	17.60	27.64	15.25	2.35	20.73	13.68	1.57	15.55	12.25	1.43	11.66	11.08	1.17	37.0	63.0
50	46.69	19.20	35.02	16.74	2.51	26.26	14.65	2.09	19.70	13.18	1.47	14.77	12.15	1.03	36.8	63.2

I.C.: Initial Concentration(µg mL^{-1}), E.C : Equilibrium Concentration (µg mL^{-1}), A.A : Amount Adsorbed (µg g^{-1}),

A.D: Amount Desorbed (µg g^{-1});C.D : Cumulative Desorbed (%), C.A :Cumulative Adsorbed (%)

Table 6. Freundlich K and n values for desorption isotherms of pendimethalin in soil.

Soil	Kf						n				
	Initial Concentration (ìg mL^{-1})						Initial Concentration (ìg mL^{-1})				
	10	20	30	40	50	Mean	10	20	30	40	50
S1	3.16	3.63	6.30	10.00	12.58	7.13	0.87	0.80	0.78	0.63	0.60
S2	2.51	3.16	4.48	6.13	9.15	5.08	0.98	0.87	0.84	0.79	0.76
S3	1.99	2.26	3.54	4.42	6.13	3.67	1.00	0.96	0.91	0.88	0.85
S4	2.81	3.98	5.01	7.07	11.22	6.02	0.81	0.76	0.65	0.61	0.55

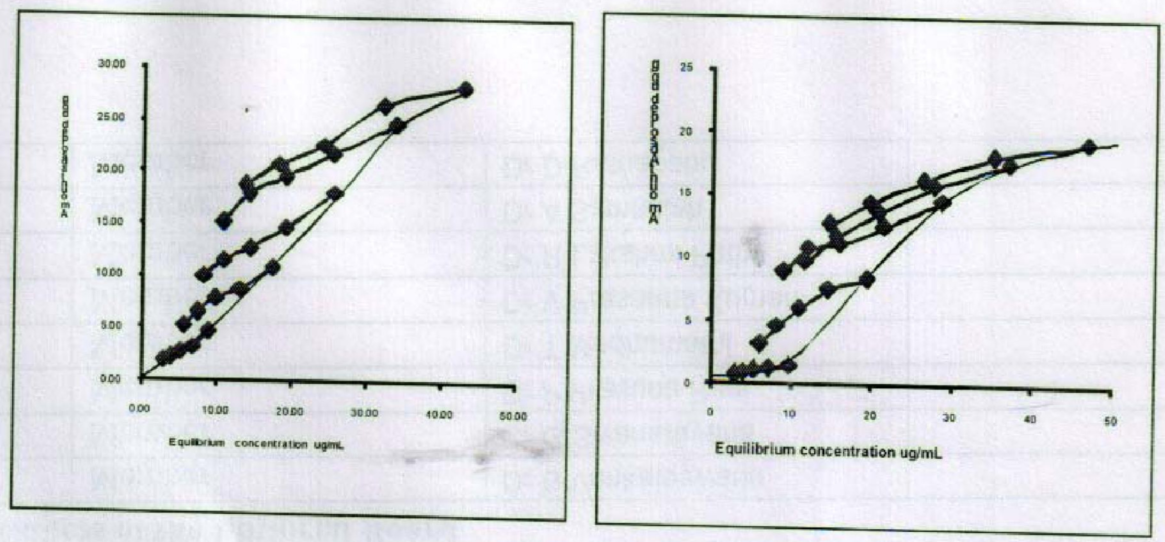

Fig. 1: Adsorption desorption isotherms of pendimethalin (Soil 1 and 2)

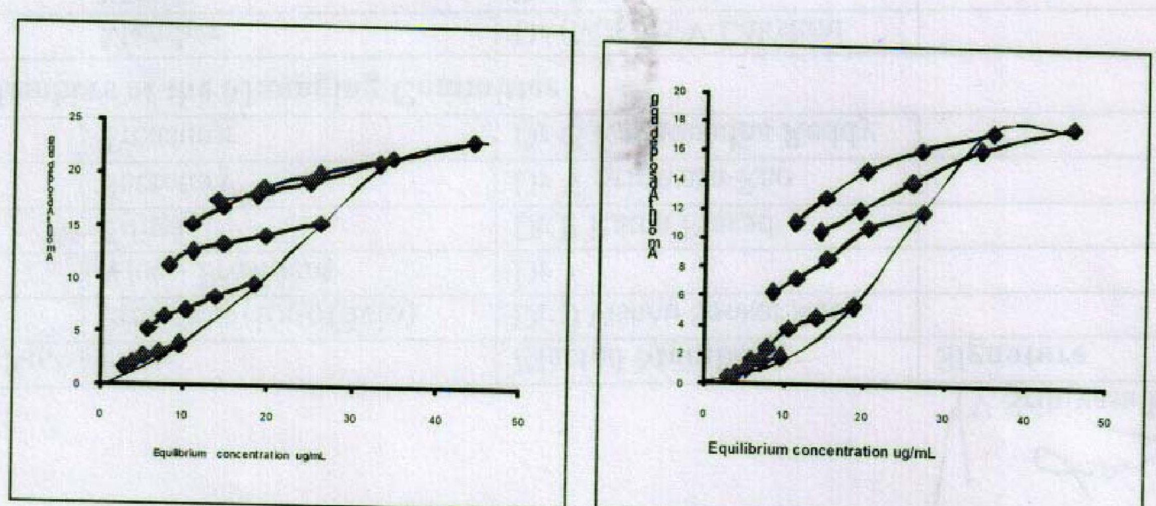

Fig. 2 : Adsorption desorption isotherms of pendimethalin (Soil 3 and 4)

Freundlich in nature and Freundlich K_f and n values are presented in Table 6 for pendimethalin. There was a consistent increase in K_f value as the initial concentration increased in all the soils. The K_f values varied from 3.16 to 12.58 in Soil 1 ; 2.51 to 9.15 in Soil 2; 1.99 to 6.13 in Soil 3 and 2.81 to 11.22 in Soil 4 with the increase in initial concentration from 10 µg mL^{-1} to 50 µg mL^{-1}. Which is an indicative of difficult desorption.

The variation in percent desorbed may be due to heterogeneity involved in different soils, that vary widely in type and energy of bonding. In general, higher amounts of herbicide was desorbed during first washing and the amount progressively decreased with each subsequent washings. The per cent cumulative desorption revealed that the adsorption of this herbicideis almost irreversible indicating that the soil organic matter and clay content plays an important role in the adsorption – desorption of pendimethalin from soil solution affecting the bio availability of herbicides in soil.

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