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Sorption Behaviour of Forchlorfenuron in Soil

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Abstract Adsorption of forchlorfenuron on three Indian soils reached equilibrium within 48 h with rate of adsorption being highest on sandy-loam followed by clay and silty-clay soils. The relative adsorptivity of the test soils could be attributed to the different organic matter and clay contents. Desorption rate followed the reverse trend. The rate constants for adsorption and desorption at 298 and 308 K were determined from Lindstrom model, which simultaneously evaluated adsorption and desorption kinetics. The data for rate constants, activation energies, enthalpy of activation, entropy of activation and free energy indicated chemical adsorption of forchlorfenuron on soil. A good fit to the linear and Freundlich isotherms was observed with correlation coefficients >0.97. The groundwater ubiquity score for different soils varied between 1.6 and 2.2, on the basis of which forchlorfenuron could be categorised as a chemical with low to medium leaching category.

Keywords Forchlorfenuron · Soil · Adsorption kinetics · Adsorption isotherm · Desorption

Forchlorfenuron is a plant growth regulator, mostly used in viticulture to improve fruit size, fruit set and cluster weight in grapes to achieve desired size and quality of table grapes as per the prescribed standards for different international markets (Ramteke et al. 2002). Use of this chemical is steadily increasing with time in terms of dose as well as application frequency. Forchlorfenuron is used as bunch dipping as well as foliar spray. Therefore, during application, a significant fraction of the applied amount may reach the soil environment and contaminate the same. This necessitates evaluating its potentiality to contaminate environment to ensure safe use. Soil is an important sink for all agricultural chemical applications. Besides, residues present in soil may re-appear in fruits through root absorption and upward translocation. It may get fractionated between soil solution phase in free form and soil solid phase through adsorption on clays and organic fraction in bounded forms while the rest might leach down to ground water. Thus, once released into soil, the adsorption and desorption behaviour of forchlorfenuron will be the major factors affecting the dynamics of its residues between sorbed and solution phases. This in turn determines the fraction to be present in solution phase, in which it is available for leaching and hence groundwater contamination. Literature survey reveals inadequacy of information about adsorption–desorption of this compound. Sharma and Awasthi (2003) reported the residue dynamics of forchlorfenuron in grape, soil and water, but they did not explore into its sorption behaviour in soil. This is the genesis of the present endeavour to report the sorption behaviour of forchlorfenuron in soils of different physicochemical properties, with the objective to assess the risk of soil and ground water contamination as a consequence of controlled or uncontrolled distribution of this chemical in soil environment.

Materials and Methods

The commercially available formulation (Swell) containing 0.1% active ingredient was selected for study.

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The certified reference standard of forchlorfenuron was purchased from Dr Ehrenstorfer GmbH, Germany (>99% purity). All the solvents and other reagents were of HPLC grade.

Three soils with different physico-chemical properties (Table 1) were selected from major grape growing areas of India. These were air-dried and sieved (<2 mm) prior to the laboratory experiment as per the USEPA designation CG-1710 (EPA 1982). The application solution was prepared by diluting Swell to different levels with 0.01 M $CaCl_2$ solution to make phase separation easier and simulate an ionic strength similar to that of a natural soil solution. Soil (10 g) and 20 mL forchlorfenuron solution were placed in 50 mL centrifuge tubes and shaken for 48 h separately at 298 ± 1 and 308 ± 1 K. Aliquots were withdrawn at 0, 0.5, 1, 3, 5, 7, 10, 24 and 48 h, centrifuged at 3,000 rpm for 20 min and the clear supernatants collected for measurements.

The adsorption isotherms were determined using five initial concentrations of 0.1, 0.5, 1.0, 10.0 and 15 mg/L with a shaking period of 48 h. The desorption study was carried out by adding an extra amount of freshly prepared 0.01 M $CaCl_2$ solution to the soil remaining in the centrifuge tubes while maintaining the total amount of the solution exactly 20 mL gravimetrically. Desorption was repeated thrice with 20 mL 0.01 M $CaCl_2$ in each case. The total amount desorbed was determined by adding the amounts for three desorption steps.

The analysis was carried out on an HPLC (Agilent 1200) hyphenated to API 4000 Q-Trap mass spectrometer equipped with ESI (+) probe. Forchlorfenuron eluted at RT of 5.72 min through a C_{18} column (220 × 4.6 mm, 5 μm). The mobile phase was composed of A—methanol:water (20:80, v/v) and B—methanol:water (90:10, v/v) with 5 mM ammonium formate in both; gradient 0–1.0 min/15%B, 1–13 min/95%B, 14–20 min/15%B. The residues were estimated by multiple reactions monitoring with mass transition 248.2$[M + H]^+$ to 129.1 with scan time of 70 ms. A second mass transition 248.2 to 155.0 was used for confirmation. The ratio of these two transitions was 0.13.

Table 1 Physicochemical properties of the test soils

Soil property	Soil I	Soil II	Soil III
Texture (%)	Sandy-loam	Clay	Silty-clay
Sand (2000–50 μm) (%)	65	21	11
Silt (<50–2 μm) (%)	18	9	47
Clay (<2 μm) (%)	17	70	42
pH (water, ratio 1:2.5)	8.0	8.5	7.0
Organic C (%)	1.07	0.81	0.15
CEC (Cmol/kg)	8.0	47.5	26.2
Maximum water holding capacity (%)	44.4	80.0	42.5
Density (g/mL)	2.2	1.9	1.5
Soil class (USDA)	Typic ustropepts	Vertic ustropepts	Typic ustochrepts

A 5-point matrix matched calibration curve was prepared (range 0.0025–0.5 mg/kg) with correlation coefficient (R^2) > 0.99. The average recoveries (±SD) at 0.01, 0.05 and 0.50 mg/kg fortification levels were 88.3 ± 9.6, 91.6 ± 5.4 and 94.2 ± 4.8%.

The fraction adsorbed was calculated as

$$\varphi(t) = (C_0 - C_t)/(C_0 - C_\infty), \tag{1}$$

where C_0 = initial concentration of forchlorfenuron in suspension, C_t = concentration after time t in suspension, C_∞ = concentration in the suspension at equilibrium and $\varphi(t)$ = fraction sorbed at time t.

The kinetics of adsorption on different soils was explored as per the following rate expression proposed by Lindstrom et al. (1970):

$$\mathrm{d}\varphi/\mathrm{d}t = k_1\left[(1-\varphi)(1-\varphi/2)\mathrm{e}^{-b\varphi}\right] + k_2\left[(1-\varphi/2)\mathrm{e}^{b(2-\varphi)} - (\varphi^2/2)\mathrm{e}^{b\varphi}\right]. \tag{2}$$

Here φ = fraction of the amount sorbed; k_1 and k_2 are the adsorption and desorption rate constants, respectively, and b a constant. The values of k_1 and k_2 were obtained from the following equations:

$$k_1\sum_1^N \left(X_i^{(1)}\right)^2 + k_2\sum_1^N X_i^{(1)} \cdot X_i^{(2)} = \sum_1^N X_i^{(1)}.Y_i, \tag{3}$$

$$k_1\sum_1^N X_i^{(1)} \cdot X_i^{(2)} = k_2\sum_1^N \left(X_i^{(2)}\right)^2 = \sum_1^N X_i^{(2)} \cdot Y_i, \tag{4}$$

where i is a running index = 1, 2, 3…N and

$$Y_i = \phi(t_0 + \ i\Delta t) - \phi t_0, \tag{5}$$

$$X_i^{(1)} = \int_{t_0}^{t_0+i\Delta t} (1-\phi)(1-\phi/2)\mathrm{e}^{-b\varphi}\,\mathrm{d}t, \tag{6}$$

$$X_i^{(2)} = \int_{t_0}^{t_0+i\Delta t} (1-\phi/2)\mathrm{e}^{-b(2-\phi)} - \phi^2/2\mathrm{e}^{b\phi}\,\mathrm{d}t \tag{7}$$

$t = (t–t_0)/N$, which is the length of each subinterval and $b = \alpha/RT$ where α is the energy stress constant for the sorbing surface. An acceptable region of b values was determined by the process of least squares as described by Bansal (2004). Y_i, $X_i^{(1)}$ and $X_i^{(2)}$ were calculated for different b values, starting with $b = 0$ and with increment of 0.25, and simultaneously, the values of φ were determined from Eqs. 2–7. The process of increasing b values by 0.25 was continued until Y_i, $X_i^{(1)}$ and $X_i^{(2)}$ gave positive values of k_1

and k_2. Out of the physically acceptable values of b thus obtained, a value was selected that gave the least value of E in the positive quadrant of $E_0 = \min E$, ($b \geq 0$, $k_1k_2 \geq 0$), in the three-dimensional vector space (k_1, k_2, b) of the equation,

$$E = \sum_{i=1}^{N} \left(Y_i - k_1 X_i^{(1)} - k_2 X_i^{(2)} \right)^2. \tag{8}$$

From the estimated values of b, the required rate constants k_1 and k_2 were obtained. The activation energy, free energy of activation, enthalpy of activation and entropy of activation were calculated with the help of rate constants for all the soils (Table 2).

Adsorption of forchlorfenuron attained equilibrium within 48 h of contact time in all the soils, after which the bound concentrations varied <5% (Langmuir 1997) between two consecutive time measurements. The adsorption–desorption data were fitted into the following linear forms of isotherm (Sundaram et al. 1995).

$$q = K_D C_e \ldots, \tag{9}$$

$$\log q = 1/n \log C_e + \log K_F \ldots, \tag{10}$$

$$1/q = 1/K_1K_2 \cdot 1/C_e + 1/K_1 \ldots. \tag{11}$$

Here $1/K_1K_2$ is the slope and $1/K_1$, the intercept of the resulting straight line. q = a variable that represents the concentration of the adsorbed compound (μg/g soil), C_e = equilibrium concentration of the test substance (μg/mL), K_D = linear or distribution adsorption constant (mL/g), $1/n$ and K_1 are the constants reflecting the adsorption strength or intensity. K_F and K_2 represent the adsorption capacity for the Freundlich and Langmuir equations, respectively. K_D is related to the soil organic carbon (OC) and soil organic matter (OM) by the following equations (Hamaker and Thompson 1972):

$$K_{OC} = 100 K_D / \%\ \text{OC}, \tag{12}$$

$$K_{OM} = 100 K_D / \%\text{OM}\ . \tag{13}$$

Since %OM/%OC = 1.724 (Beulke and Brown 2001), K_{OC} can be calculated by the following equation:

$$K_{OC} = 1.724 K_{OM}. \tag{14}$$

Results and Discussion

The rate of adsorption followed the order sandy-loam > clay > silty-clay, which may be due to the combined effect of OM and clay contents of the soils. The higher values of k_1 than k_2 indicated that adsorption is always preferable to desorption. The value of ΔG_a for adsorption was lower than that of desorption; the higher the value of ΔG_a at a particular temperature slower is the reaction rate. ΔG_a

Table 2 Kinetic parameters for adsorption–desorption process

Soil	Temperature	b-value	Rate constant (s^{-1})		E_a (kJ/mol)		ΔH (kJ/mol)		ΔS_a [kJ/(mol deg)]		ΔG_a [kJ/(mol deg)]	
			Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
Sandy loam	298	4.25	2.62×10^{-3}	1.72×10^{-9}	118	−29	116	−31	0.08	−0.53	91	127.2
	308	6.00	1.23×10^{-2}	1.18×10^{-9}	118	−29	115	−31	0.09	−0.52	87	128.2
Clay	298	2.25	4.17×10^{-4}	1.34×10^{-7}	167	−230	164	−233	0.24	−1.16	92	112.2
	308	4.75	3.71×10^{-3}	6.57×10^{-9}	167	−230	164	−233	0.24	−1.16	90	123.8
Silty clay	298	1.50	2.33×10^{-4}	1.25×10^{-7}	178	−62	176	−65	0.27	−0.59	93	112.4
	308	4.00	2.4×10^{-3}	5.52×10^{-8}	178	−62	175	−65	0.27	−0.59	91	118.3

followed the order sandy-loam < clay < silty-clay. The enthalpies of activation (ΔH_a) for adsorption was higher than that of desorption since with rise in temperature adsorption increased but desorption decreased. The values of ΔH_a for adsorption pointed towards chemisorption, and hence this may be the reason that desorption rate decreased with rise in temperature, due to chemical adsorption on soil. The values of ΔS_a for adsorption were positive, indicating that the formation of an activated complex via co-ordination or association is not favoured. Negative values of ΔS_a for desorption were due to the forchlorfenuron soil complex becoming activated before desorption. The values of E_a, $\Delta G_{a,}$ ΔH_a and ΔS_a also supported the rate of adsorption of forchlorfenuron on soil as sandy-loam > clay > silty-clay. Thus it can be hypothesised that the adsorption of forchlorfenuron on soil is chemical in nature with the formation of a bound complex that discourages desorption with rise in temperature. This lays foundation in studying the aspects of the nature of chemical bond formed during adsorption of forchlorfenuron on soil surface in future attempts.

Adsorption occurred in two phases. The first phase had a rapid mass transfer from the aqueous phase to the adsorbing sites, followed by a slow phase, which might be due to the requirement of more energy for adsorption in less accessible sites. The extents of adsorption–desorption in different soils with regards to the amount applied are presented in Table 3.

A good fit to the linear and Freundlich isotherms was observed. For the Langmuir model, as the parameters K_1 and K_2 were negative (Table 4), it could not explain the adsorption process (Bailey and White 1970). The non-applicability of the Langmuir equation to the results might be due to the heterogeneity and surface acidity of these soils. Furthermore, the Langmuir isotherms are generally observed when there is enough of a chemical to form multiple layers on the solid surfaces. In the present studies the concentration of forchlorfenuron was quite low and this may be the reason why this model did not work.

Table 3 Adsorption–desorption of forchlorfenuron in soils

Soil	Amount applied (μg)	Total adsorbed (μg)	Adsorbed (%)	Amount desorbed (μg)	Adsorbed amount desorbed (%)
Sandy-loam	300	272.5	90.8	9.0	3.3
	200	185.3	92.6	5.9	3.2
	100	94.3	94.3	3.2	3.4
	20	18.9	94.5	0.48	2.5
	2	1.9	95.0	0.08	4.2
Clay	300	270.8	90.3	20.3	7.5
	200	179.6	89.8	12.5	7.0
	100	90.1	90.1	6.3	7.0
	20	19.6	98.0	1.0	7.8
	2	1.9	95.0	0.15	4.2
Silty-clay	300	249.7	83.2	28.0	11.2
	200	174.5	87.3	17.3	9.9
	100	87.8	87.8	8.6	9.8
	20	19.4	97.0	1.6	8.2
	2	1.9	95.0	0.15	7.9

The linear adsorption coefficient K_D was highest in sandy-loam, followed by clay and silty-clay soils, respectively (Table 4). The higher K_D in the sandy-loam and clay soils may be attributed to the higher OM and clay contents in these soils as compared to the silty-clay soil (Koskinen and Harper 1990). This finding is furthermore supported by the higher K_{OC} value observed for the silty-clay soil. The K_{OC} values suggest that adsorption of forchlorfenuron in the test soils is generally strong indicating low leaching potential. The higher K_D in sandy-loam soil indicates greater adsorption than in clay and silty-clay soil, which may be attributed to the higher OM contents in it, indicating interaction of forchlorfenuron molecules with organic fraction of the soils. The leaching potential of forchlorfenuron was estimated by using the following empirical model of Gustafson (1993), which predicts the leaching potential of a test compound in terms of the groundwater ubiquity score (GUS) as described by the following equation. $\text{GUS} = \log(\text{DT}_{50}) \times [4 - \log(K_{OC})]$. As per this model, a chemical with GUS > 2.8 is considered to be of high leaching potential, whereas, if the GUS < 1.8, it is supposed to be of low leaching compound. Half-life (DT_{50}) of forchlorfenuron for all the test soils as determined in separate experiments for sandy-loam, clay and silty-clay soil at 60% of maximum water holding capacity were 4, 6.3 and 10 days, respectively. The GUS for the sandy-loam, clay and silty-clay soils were found to be 1.6, 2.1 and 2.2, respectively. Hence, forchlorfenuron is considered to be a chemical belonging to the low to medium leaching potential category.

The K_F values also followed similar pattern as the K_D indicating highest amount of adsorption at an equilibrium concentration of 1 mg/L in sandy-loam soil as per the Freundlich model (Table 4). The results are in agreement with the difference in Freundlich parameter $1/n$, which indicates the degree of non-linearity in an isotherm. The adsorption isotherm in clay soil was almost linear. In sandy-loam and silty-clay soils, *L*-type isotherm was observed ($1/n < 1$) indicating higher affinity of forchlorfenuron to the adsorbing sites at low concentration. There was a reducing trend in the extent of adsorption against the increase in forchlorfenuron concentration.

Desorption of forchlorfenuron increased as sandy-loam < clay < silty-clay, which is opposite to the order

Table 4 Adsorption parameters of forchlorfenuron in different soils

Model	Parameter	Before desorption			After desorption		
		Sandy-loam	Clay	Silty-clay	Sandy-loam	Clay	Silty-clay
Freundlich	K_F	24.6	19.0	14.2	63.6	27.1	21.4
	$1/n$	0.88	1.03	0.72	1.03	1.0	0.93
	N	1.09	1.25	1.38	0.97	0.99	1.07
	R^2	0.99	0.99	0.97	0.99	0.99	0.99
Langmuir	$1/K_1$	−0.002	−0.21	0.01	−0.09	−0.09	−0.06
	K_1	−489.8	−4.8	−0.008	−10.1	−11.3	−15.3
	$1/K_1K_2$	0.03	0.04	0.02	0.02	0.04	0.04
	K_2	−0.07	−5.9	−0.38	−4.5	−1.96	−1.57
	R^2	0.99	0.94	0.99	0.99	0.99	0.99
Linear	K_D	20.1	17.9	10.1	58.6	24.8	15.3
	K_{OC}	18.8	22.1	67.4	54.8	30.6	101.9
	K_{OM}	10.9	12.8	39.1	31.8	17.7	59.1
	R^2	0.97	0.99	0.97	0.99	0.99	0.95

with which the extent of adsorption varied among the test soils (Table 4). Desorption conformed to the Freundlich and Langmuir isotherms in all the three soils (Table 4). The K_D values pertaining to desorption were consistently higher than the corresponding values for adsorption. Such a phenomenon might have occurred due to a possible hysteresis effect during desorption involving various forces that caused higher retention of forchlorfenuron molecules after desorption than that of adsorption at unit equilibrium concentration. Furthermore, such observations indicate that the process of adsorption was reversible.

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