

Effect of Temperature on Adsorption-Desorption of Isoproturon on a Clay Soil

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ABSTRACT

The present investigation was undertaken to study the effects of temperature on adsorption-desorption of isoproturon on a clay soil and fit the data obtained to Freundlich adsorption-desorption isotherm model. The adsorption curves revealed that adsorption of isoproturon conformed to a L-type adsorption isotherm at the higher temperature (20°C), while a S-type at lower temperature (10°C). The adsorption of isoproturon decreased with the increase in temperature, indicating the exothermic nature of adsorption reactions. The phenomenon of hysteresis appeared to be more pronounced at lower temperature than at higher temperature.

INTRODUCTION

Isoproturon [3-(4-isopropyl phenyl)-1, 1-dimethyl urea] is one of the most commonly soil applied phenyl urea herbicides for controlling annual grass weeds like *Phalaris minor* in wheat (Feilding *et al.*, 1994). The adsorption-desorption behaviour of soil applied pesticides is one of the most important factors governing their bioefficacy and persistence. The pesticide present in soil solution is bioavailable and may also be subjected to various dissipation processes such as degradation, volatilization and leaching. The adsorbed pesticide is not immediately available for these processes. However, the adsorbed pesticide, which is in equilibrium with soil solution pesticide, would be partially desorbed when the concentration in the soil solution decreases (Gajbhiye and Gupta, 2001). Adsorption equilibrium is affected by the chemical structure of the compound, nature of the organic and inorganic colloidal fractions of the soil and the environmental factors (Maria and Sanchez, 1991). Precipitation and temperature are two very important climatic factors, which influence adsorption (Yaron and Saltzman, 1972). In view of the above mentioned points, the present investigation was undertaken with the objective

to see the effect of temperature on adsorption-desorption of isoproturon on a clay soil.

MATERIALS AND METHODS

Soil sample for the present investigation was collected from Rampur. It was dried in shade, crushed with a wooden roller, passed through a sieve having an opening on 0.850 mm diameter and then analyzed for its general properties like soil pH, soil organic carbon, water holding capacity, specific electrical conductivity, calcium carbonate content, cation exchange capacity and mechanical analysis (Table 1).

A stock solution of 100 ppm isoproturon was prepared in 0.01M CaCl₂. 2H₂O solution by initially dissolving it in a small amount of methanol. Serial dilutions of varying concentrations viz., 0, 5, 10, 20, 30 and 50 ppm were prepared by diluting the stock solution with 0.01 M CaCl₂. 2H₂O solution. The λ_{max} was determined by UV-VIS spectrophotometer and was found to be 226.5 nm. Absorbance for each concentration was determined by the spectrophotometer and a calibration curve was plotted between absorbance and concentration. Equilibration time for adsorption was determined by taking one gram soil sample and 10 ml of

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Table 1. Some general properties of soil samples used in the study

Properties	
Soil textural class	Clay
Water holding capacity (%)	50.98
pH (1 : 2, soil : water suspension)	7.95
Electrical conductivity (dSm ⁻¹) (1 : 2, soil : water suspension)	0.69
Cation exchange capacity (cmol (p ⁺) kg ⁻¹ soil)	28.28
Organic carbon content (g kg ⁻¹)	4.8
CaCO ₃ content (g kg ⁻¹)	6.82

isoproturon solution of concentration (0, 5, 10, 20, 30 and 50 ppm) in centrifuge tubes. The soil samples were kept for shaking on a shaker for 2 h and then incubated in an incubator at different temperatures (10 and 20°C) for different time periods. The equilibration time was found to be 24 h.

The contents of the tubes after equilibration were centrifuged to obtain a clear supernatant. The clear supernatant was stored in plastic vials and the absorbance of each supernatant was obtained against blank at 226.5 nm on the UV-VIS spectrophotometer. The amount of isoproturon adsorbed was calculated as the difference in concentration of isoproturon in the initial and final solution after equilibration.

The adsorption data were fitted to a Freundlich adsorption isotherm model.

$$x/m = KC_e^{1/n}$$

$$\log x/m = \log K + 1/n \log C_e$$

Where,

x/m = Amount of isoproturon adsorbed per unit mass of soil (mg/kg)

C_e = Equilibration concentration of isoproturon (mg/L)

K and n = Empirical constants

Desorption studies were also carried out on soil sample to which 50 ppm isoproturon solution was added for adsorption study. After the decantation of supernatant, the soil pellet remaining in the centrifuge tube was dispersed in 10 ml of 0.01 M CaCl₂·2H₂O. The contents were thoroughly mixed and care was taken that no soil remained sticking to the tubes. A blank was run side by side. The tubes were kept for shaking for 2 h and then incubated at different temperatures (10 and 20°C) for 24 h.

These tubes were centrifuged to obtain a clear

supernatant. The absorption of the supernatant was determined at 226.5 nm against blank on UV-VIS spectrophotometer. The process was repeated till detectable concentration of isoproturon was present in the supernatant.

RESULTS AND DISCUSSION

A calibration curve of isoproturon plotted between concentration and absorbance at λ_{max} followed a perfect linearity and was used for computing the concentration of isoproturon in the equilibrium solutions from adsorption and desorption studies (Fig. 1).

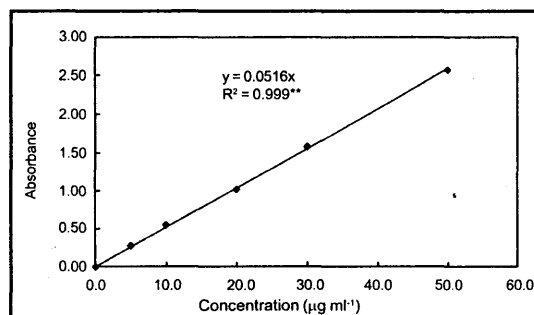


Fig. 1. Calibration curve of isoproturon at 226.5 nm.

It is evident from Fig. 2 that at both the temperatures (10° and 20°C), the adsorption of isoproturon increased with increasing concentration of herbicide. The shape of the adsorption curve revealed that isoproturon adsorption at higher temperature (20°C) conformed to a L-type adsorption isotherm (Giles *et al.*, 1960) indicating increasing competition offered by the solvent molecules for adsorption surfaces, while at lower temperature (10°C) the adsorption isotherm was S-type implying

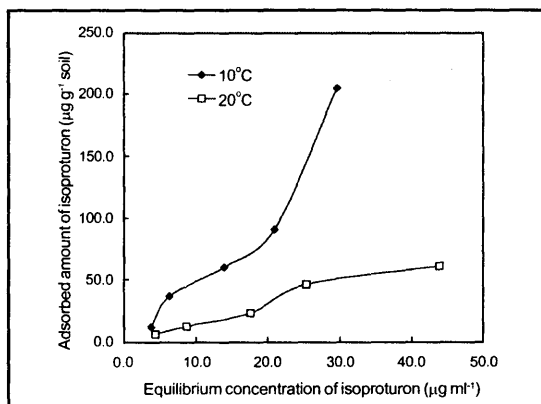


Fig. 2. Effect of temperature on adsorption of isoproturon on a clay soil.

Table 2. Freundlich adsorption parameters of isoproturon at 10° and 20°C temperature

Temperature (°C)	Log K	1/n	R ² value
10	0.4642	1.2025	0.947**
20	0.1750	1.0046	0.983**

**Significant at P=0.05.

side by side association between adsorbed molecules or cooperative adsorption, which might be attributed to multiplayer adsorption involving van der Waal forces.

The adsorption of isoproturon decreased with the increase in temperature from 10° to 20°C indicating exothermic nature of adsorption (Kumar *et al.*, 1987; Mandal and Adhikari, 1995). The adsorption data conformed well to Freundlich adsorption isotherm (Fig. 3), the values of coefficient of determination (R²) were 0.947 and

0.983 at 10° and 20°C, respectively, which were statistically significant at P=0.05. The values of adsorption capacities at 10° and 20°C temperatures revealed that an increase in temperature brought a pronounced decrease in adsorption capacity of isoproturon on clay soil (Table 2). The value of slope factor or order of adsorption (1/n) was close to unity indicating thereby involvement of adsorption sites of higher adsorption energies (Raman and Reddy, 1987).

As evident from the data presented in Table 3, the desorption of isoproturon gradually decreased during sequential desorptions. As regards the effect of temperature on desorption of isoproturon, it was found that although the initial adsorbed quantity of isoproturon on clay soil was lower at 20°C as compared to 10°C yet the desorption was

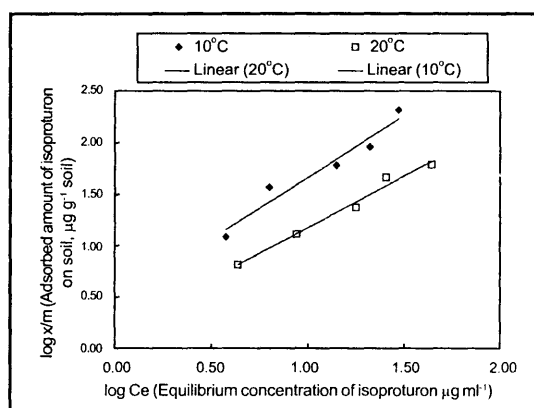


Fig. 3. Freundlich adsorption isotherms of isoproturon on a clay soil at 10 and 20°C temperatures.

Table 3. Sequential desorption data of isoproturon at 10° and 20°C temperature on a clay soil

Temperature (°C)	Initial adsorbed amount of isoproturon (µg g ⁻¹ soil)	Concentration of isoproturon in equilibrium solution (µg ml ⁻¹)	Adsorbed amount of isoproturon (µg g ⁻¹ soil)
10	204.82	9.54	109.38
		1.91	90.23
		0.74	82.81
		0.33	79.56
20	61.92	4.71	14.81
		0.91	5.75
		0.07	5.00

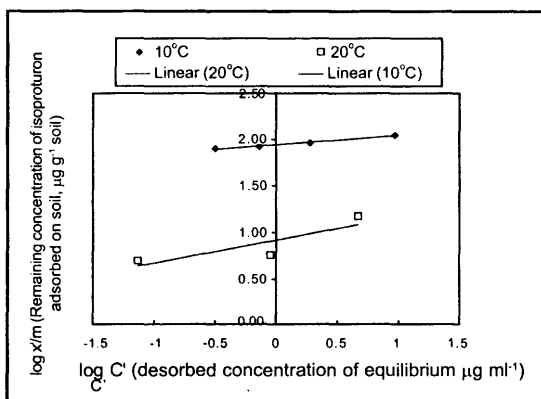


Fig. 4. Freundlich desorption isotherms of isoproturon on a clay soil at 10° and 20°C temperatures.

proportionately higher at higher temperature.

Bailey and White (1970) had also reported that desorption processes were endothermic in nature and an increase in temperature would normally be expected to favour the desorption process. Desorption data of isoproturon fitted well to Freundlich desorption isotherm model (Fig. 4). The desorption capacity of isoproturon decreased with the increase in temperature, while the slope factor ($1/n'$) increased with increase in temperature (Table 4).

Table 4. Freundlich desorption parameters of isoproturon at 10° and 20°C temperature

Temperature (°C)	Log K'	$1/n'$	R ² value
10	1.9377	0.0964	0.975**
20	0.9171	0.2446	0.749**

**Significant at P=0.05.

Desorption index value calculated as ratio of slope factors for adsorption and desorption processes (n'/n) was found to be 12.47 and 4.11 at 10° and 20°C, respectively. Desorption index value greater than unity indicated that the phenomenon of hysteresis occurred during desorption process. Desorption hysteresis has been reported for interaction of a large number of organic compounds

with soils and ascribed to several reasons like chemical or biological transformations, non-equilibrium conditions and high energy bonding (Pavlostathis and Matharan, 1992). It appeared that a fraction of adsorbed isoproturon remained strongly bound to soil. Only the fractions of herbicide weakly bound to soil could be released during desorption.

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