A New Method for Determination of Adsorption and Desorption Coefficients of Pesticides with Soil Column Liquid Chromatography

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Abstract: The adsorption and desorption coefficients of atrazine, methiocarb and simazine on a sandy loam soil were measured in this study with soil column liquid chromatographic (SCLC) technique. The adsorption and desorption data of all the three pesticides followed Freundlich isotherms revealing the existence of hysteresis. In comparing with other methods, SCLC method showed some characteristics such as rapidity, online and accuracy.

Keywords: Adsorption, desorption, pesticides, soil column.

Agricultural chemicals such as pesticides were extensively applied in the fields. Pesticides effectively protect the crops, only as long as they remain in the root zone of soil. In case a portion of the chemicals leaves root zone and especially leaches through soil pores. They may pollute groundwater and be a serious environmental problem[1]. This problem has got widespread concern in the world. In soils the fate of organic compounds such as pesticides is governed by hydraulic transport coupled with adsorption, desorption and degradation processes. To interpret the mechanism of adsorption and desorption is difficult because of the heterogeneity of natural soil components[2].

Earlier studies of the uptake of chemicals by soil from groundwater have indicated that soil organic matter is the principal adsorbent. And it has been speculated that the high surface area of this organic matter is an important factor[3]. The soil organic carbon adsorption coefficient (K_{oc}) of a chemical is defined as:

$$K_{oc} = K_d / f_{oc} \qquad (1)$$

where f_{oc} is the soil organic carbon fraction (expressed in grams per gram soil) and K_d is the distribution coefficient. Among the mathematical models of adsorption proposed so far, the Freundlich isotherm is the one most frequently used to describe adsorption processes. It assumes that heterogeneous distribution of the fixation sites without saturation of soil surface is more likely to occur in chemical / soil systems. *i.e.*

$$K_d = C_s / C_e^{1/n} \qquad (2)$$

where C_s (micrograms per gram soil) is the concentration of the chemical adsorbed onto the soil, C_e (milligrams per liter) is the concentration in the soil solution, and n is a dimensionless exponent.

Besides adsorption, the desorption process also plays an important role in the behavior of a chemical in field soil. And desorption data also well conform to Freundlich isotherm equation. Moreover hysteresis and irreversible bound of chemicals to soil have been reported elsewhere[4,5]. Hysteresis is quantified as:

$$\omega = n_{des} / n_{ads} - 1 \qquad (3)$$

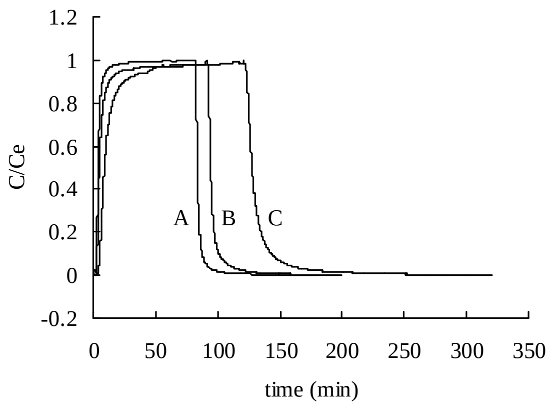
where n_{ads} and n_{des} are dimensionless exponent of adsorption and desorption isotherms respectively.

Atrazine, methiocarb, and simazine are all widely used in modern agriculture. It is very significant to grasp their respective adsorption and desorption behavior on soil. It offers useful and important information about processes for involvement of pesticides in the environment.

The batch equilibrium technique has been recommended in OECD Guidelines to measure adsorption and desorption coefficients of chemicals[6]. Several studies have reported the determination for adsorption and desorption of chemicals, mainly atrazine and its metabolities[7,8], and other pesticides[9-12]. The objective of this paper is to develop an alternative method to study such environmental behavior by using soil packed column.

The soil used for this study was SP 30697 sandy loam soil from LUFA Speyer, Germany. Before being packed into the column (100×i.d. 5 mm), soil was air dried at ambient temperature and sieved to a particle size from 60 to 80 mesh. The purities of the three test pesticides were more than 99%.

Figure 1 The breakthrough curve for adsorption of atrazine (A) 20 mg/L, methiocarb (B) 5 mg/L, and simazine (C) 15 mg/L and desorption eluted with pure water



Adsorption isotherm of each pesticide involved at least six points, each of which was replicated. The aqueous solutions of pesticides (C_e) were used as the mobile phase at a flow rate of 0.2 mL/min. The water solubilities of atrazine, methiocarb, and simazine were 30, 27 and 6.2 mg/L respectively. So the solution concentrations chosen in this study ranged approximately from 81 to 2% of the pesticide water solubility. The equilibrium attained when the effluent had the same concentration as C_e. The adsorption amount of pesticides from water can be calculated through breakthrough curves (BTCs).

After the adsorption equilibrium reached at a certain concentration, the sorbed pesticide on soil was eluted with pure water (**Figure 1**) or a lower concentration solution. In this study the desorption experiments were performed in five or six successive steps, while each experiment was run in duplicate. The areas above and below the BTCs, after subtracting with the dead time of the HPLC system, represent the adsorption and desorption amount of the pesticide respectively.

Table 1 Regression coefficients for adsorption and desorption of atrazine, methiocarb, and simazine on Sp 30697 soil

Pesticides	K_{ads}	n_{ads}	r	$logK_{oc}$	K_{des}	n_{des}	r	ω
atrazine	1.934	1.31	0.9981	2.19	4.456	2.01	0.9991	0.534
methiocarb	5.484	1.43	0.9993	2.65	12.88	2.66	0.9913	0.860
simazine	1.653	1.27	0.9981	2.12	2.933	2.47	0.9982	0.945

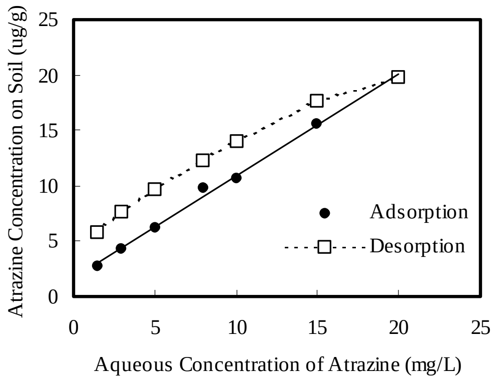
The Freundlich adsorption constant (K_{des}) demonstrates the degree or strength of adsorption isotherm. When n is equal or close to 1, adsorption would be linearly proportional to the equilibrium solution concentration and thus, a distribution coefficient (K_d) would be more appropriate for use. To distinguish them from the coefficients of desorption isotherms, K_{ads} and n_{ads} were used in this study. The values for atrazine, methiocarb and simazine are reported in **Table 1**.

The n_{ads} for adsorption of atrazine, methiocarb, and simazine were 1.31, 1.43 and 1.38 respectively. It revealed the heterogeneous distribution of the fixation sites without saturation of soil surface. The $logK_{oc}$ values were atrazine 2.19, methiocarb 2.65, and simazine 2.12 respectively (**Table 1**). The conclusion can be got that the mobility of pesticides in soil-water system decreased in the following order simazine > atrazine > methiocarb.

The desorption isotherms of atrazine, methicarb, simazine were described by Freundlich equation as well as their adsorption ones (atrazine, **Figure 2**). The n_{des} of all the isotherms were more than their respective n_{ads} values, indicating the presence of hysteresis (**Table 1**).

Both the adsorption and desoprtion of pesticides are well described by Freundlich isotherm. The relationship of $n_{des} > n_{ads}$ revealed the existence of hysteresis in the process of adsorption and desorption. It can be concluded that the adsorption is irreversible. And as an alternative method, this method is easy to operate in laboratories. This method can shorten the run time of the experiment and decreases the liability of pesticide degradation in the soil-water system.

Figure 2 Adsorption and desorption isotherms for atrazine on Sp 30697 soil



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Refenrences

1. M. Flury, *J. Environ. Qual.*, **1996**, *25*, 25.
2. C. Moreau – Kervevan, C. Mouvert, *J. Environ. Qual.*, **1998**, *27*, 46.
3. C. T. Chiou, L. J. Peters, V. H. Freed, *Science*, **1979**, *206*, 831.
4. L. Ma, L. M. Southwick, G. H. Willis, H. M. Selim, *Weed Sci.*, **1993**, *41*, 627.
5. C. A. Seybold, W. Mersie, *J. Environ. Qual.*, **1996**, *25*, 1179.
6. *OECD* Guidelines for testing of chemicals, TG 106 adsorption – desorption in soils, Paris, **1981**.
7. W. Mersie, C. Seybold, *J. Agric. Food Chem.*, **1996**, *44*, 1925.
8. C. Moreau, C. Mouvet, *J. Environ. Qual.*, **1997**, *26*, 416.
9. J. M. Gonzalez, L. Ukrainczyk, *J. Environ. Qual.*, **1996**, *25*, 1186.
10. A. Carton, T. Isla, J. Alvarez-Benedi, *J. Agric. Food Chem.*, **1997**, *45*, 1454.
11. S. A. Clay, R. R. Allmaras, W. C. Koskinen, D. L. Wyse, *J. Environ. Qual.*, **1988**, *17*, 719.
12. C. M. Fouque-Brouard, J. M. Fournier, *Talanta*, **1996**, *43*, 1793.

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