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Model Isothermal Of The Equilibrium Of The Herbicide 2,4-Dichlorophenoxyacetic Acid In Watery Phase On Soil With High Contained Organic Matter

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ABSTRACT

Adsorption isotherm of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide on soil high in organic matter (used in rice cultivation) from determined batch test. The effects of contact time, initial concentration were investigated. The adsorption equilibrium data were processed in accordance with three most widely used adsorption isoterms: Freundlich, Langmuir and Temkin isoterm models. The equilibrium data were best represented by Freundlich isoterm model, showing higher Kd values reveal that adsorption is strong. These results are related to the different content and nature of soil organic matter.

Keywords: Herbicide, contamination, water, adsorption isotherm.

Introduction

The retention is one of the first phenomena to which pesticides are subjected upon arrival to soils. The retention has an important influence on the fate of pesticides and other organic compounds, including their mobility and bioavailability in soils (Calvet, R., 1981; Chassin & Calvet, 1985).

Adsorption is defined as the passage of a liquid phase solute (soil solution) to solid-liquid interfaces of soil (Calvet, R., 1989; Calvet R., 1988). It is a reversible process which involves the attraction of the compound to the surface of the soil particle for a time that depends on the affinity of the compound for the surface.

In the soil, the adsorption corresponds to a dynamic phenomenon of partition of a solute of a liquid phase, the solution of the soil, towards a solid phase, the group of particles that constitute the matrix organomineral (Kolpin *et a,l* 1998; Neumann *et al*, 2002). Most of the work shows that the adsorption is a fast phenomenon where some hours are usually sufficient to reach equilibrium. However, in some systems, the balance may on occasion require a longer time (Weber *et al*, 2001).

The adsorption of pesticides in soils depends on the physicochemical characteristics of the molecules such as hydrophobicity, water solubility and electronic structure and soil properties and in particular their different constituents. Soil constituents have higher sorption capacity are inorganic and organic matter, and it is difficult to clearly separate their roles because they are often closely associated (Calvet, R., 1989; Hamaker & Thompson, 1972; Chiou *et al*, 1979).

The 2,4-dichlorophenoxyacetic acid (2.4-D) are used effectively for control of weeds (Salman & Al-Saad, 2012). Also, this compound is one of the oldest herbicides used in the world, and today continues to be one of the most commonly used in the market (http//www.eartportal.org/news/?p=396). The half life of 2,4-D in the environment is relatively short, averaging 10 days in soils and less than ten days in water, but can be significantly longer in cold, dry soil, or where the appropriate microbial community is not present to facilitate degradation (Salman & Al-Saad, 2012).

However, recent studies detected that the physicochemical properties of the water had a great influence on herbicide persistence of 2,4-D in water where the values of half-life greater than 10 days (Romero JM, 2014).

Since nothing is knows about the fate of 2,4-D in soil high Paraná areas used in rice cultivation in this paper a study of adsorption processes in soil with high organic content, this will could indicate the persistence of this herbicide in the environment.

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Experimental

Preparation of soil

The soils used in the study come from a site near the rice planting area of high Parana, located in the town of Itati 27°16′0″S 58°15′0″O. Sampling was collected in the winter of 2013 at different depths to differentiate the horizons affected by the work of the soil or for the installation of a vegetable permanent cover. We worked with the samples as a whole without discriminating depth.

In general, the soil used in the study are brown hydromorphic silt loam texture, 22% clay, 46% silt and 32% sand, most important, is the high content of organic matter (OM).

The samples must be conditioned in glass flasks of broad mouth and preserves up to 4°C for analysis. Before the experiment, the samples dry off and pass through a sieve to retain soil particles less than 2 mm.

Herbicide 2,4-D

2,4-dichlorophenoxyacetic acid (2.4-D) CAS N 94-75-7 supplied by Sigma–Aldrich was used as an adsorbate. Deionized water was used to prepare all the solutions and reagents. Solution of 2,4-D of 1080 ppm was prepared from which the dilutions used were obtained.

Batch equilibrium studies

Forty-milliliter aliquots of aqueous solutions that contained increasing concentrations of the 2.4-D compounds were added to 1g portions of the soil in 125 mL flasks. 2,4-D concentrations ranged from 40.0 to 120.0 mg/L. The pH of the soil suspensions was .6.8 the original without any pH adjustment. The flasks were agitated continuously on a laboratory shaker at room temperature (25 °C± 1°C.) for 24 hours. The soils were separated then by high speed centrifugation for 20 minutes and the equilibrium concentration of each 2:4-D compound was determined in the supernatant by HPLC method.

Methods for determining the sorbed concentration (Cs), concentration equilibrium (Ce)

The sorbed concentration (Cs), expressed in mg kg^{-1} soil was calculated by the difference between the concentration the initial solution added (Ci, mg L^{-1}) and the concentration of the solution of in equilibrium with the soil (Ce, mg L^{-1}):

$$Cs = (Ci - Ce)\ (V / M)$$

Where V is the volume of the solution (L) and M is the Soil amount (kg).

Equilibrium models

Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm is given in equation (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_n} + \frac{1}{K_L q_e} \qquad (1)$$

Where C_e is the equilibrium concentration (mg/L); q_e is the amount 2,4-D adsorbed at equilibrium (mg/g); q_m is the adsorption for complete monolayer (mg/g) and K_L is the sorption equilibrium constant (L/mg).

Freundlich isotherm

Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \qquad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants with n giving an indication of how favorable is the adsorption process. K_f (mg/g (L/mg) 1/n) is the adsorption capacity of the adsorbent, which can be defined as the adsorption or distribution coefficient and represents the quantity of herbicide adsorbed onto activated carbon for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption.

Temkin isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The Temkin isotherm has been used in the form as follows:

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$$q_e = B \ln A + B \ln C_e \qquad (3)$$

Where B = RT/b, b is the Temkin constant related to heat of sorption; A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K).

Results and Discussion

Determination of equilibrium parameters

We analyzed three equilibrium models: Freundlich, Langmuir and Temkin. Likewise, we determined equilibrium parameters of these models through the minimization of the difference between the amounts of pesticide absorbed experimentally and calculated according to the model, using the Microsoft EXCEL SOLVER.

Adsorption isotherm is a functional expression that correlated the amount of solute adsorbed per unit amount of the adsorbent and the concentration of adsorbate in bulk solution at given temperature under equilibrium conditions.

Determination of equilibrium models

We analyzed three equilibrium models. Figure 1 shows the correspondence between the values of the concentration in the liquid phase obtained experimentally and calculated according to the model considered, for the system studied. Seen that as the concentration increases the amount adsorbed increases but there comes a concentration at which there is no appreciable increase is 1080 ppm.

Figure 1 show these models and may note that Freunlich isotherm is that best fits to the adsorption of the herbicide in the soil in particular.

The applicability of the isotherm models to fit the adsorption data was compared by judging the correlation coefficients, R^2 values. The closer the R^2 value to unity is better the fit. The analysis of the isotherm data was done by fitting them these isotherm models to find the suitable model that can be used for design purposes.

The adsorption isotherm parameters values obtained for adsorption of 2,4-D on the soil at 25ºC are listed in Table 1.

Table 1: Freundlich, Langmuir and Temkin isotherm model parameters and correlation coefficients

	Freundlich			Langmuir			Temkin		
	K_f $(L/g)^{1/n}$	1/n	R^2	q_m (mg/g)	K_L (L/mg)	R^2	A (L/g)	B	R^2
Soil	18.89	0.29	0.992	148.36	0.015	0.979	0.29	23.28	0.955

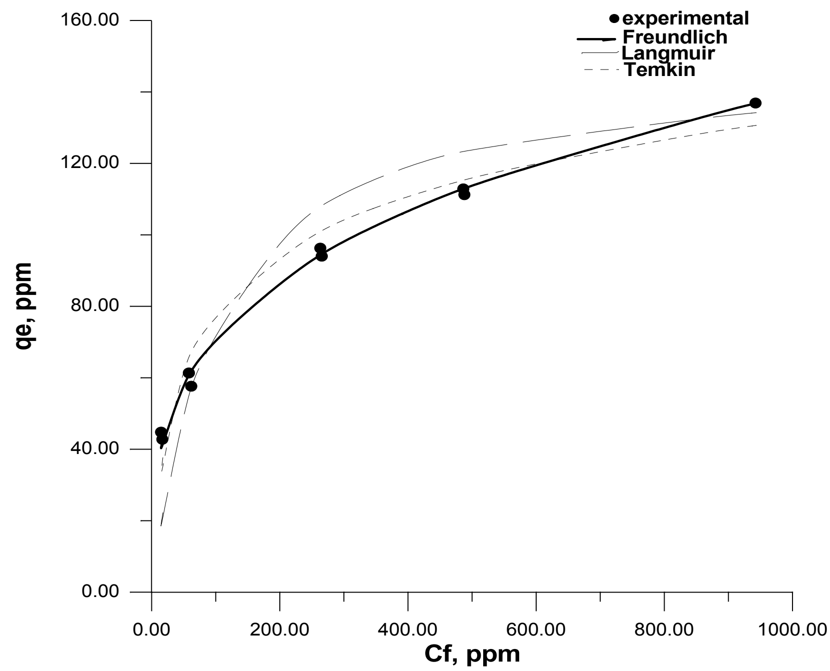

Figure 1: Experimental values according to equilibrium and non-isothermal prediction model adsorption system for the herbicide 2,4 D in soil

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According to the proposal by Giles *et al* (1960) isotherms with smaller values of 1 / n defines an isotherm of type L, indicating a decrease of the adsorption sites with increasing concentration. The K_f high value significantly and positively correlates with the carbon content, demonstrating that the organic material is a important factor for adsorption.

According to Torrents *et al* (1997), the herbicides of the group of phenoxyacid can be adsorbed in the organic matter by means of forces Van Der Waal between the aromatic ring and aromatic rings of the surface of the organic matter and bridges of links of hydrogen between the oxygen of carbonyl of the acid group of herbicide and the carboxylic hydrogen and groups hidroxílicos present in surface of the organic matter.

Procedures to determine the sorption coefficient normalized organic carbon (kfoc), the potential for leaching (GUS)

The sorption constant normalized organic carbon (K_{foc}) was calculated utilizing an K_f in the expression:

$$K_{foc} = (k_f / \% CO) \times 100$$

For 2,4-D classification regarding their potential for leaching an index was proposed by Gustafson (1989):

$$GUS = \log t1 / 2 (4 - \log k_{foc})$$

In concordance to value of K_{fco} 293 L/g obtained we can say that the high content of organic matter is responsible for the high adsorption of 2,4-D.

The GUS index value of 3.2 indicates that 2,4-D tends to leach.

Conclusion

According to the results obtained it was possible to determine various kinds of parameters from the three adsorption models, and Freundlich is leading to a mean relative error small (1-7%), similar to the experimental error.

However, the other two models have sufficient accuracy and could be considered physically accurate: Langmuir and Temkin. The Freundlich model is the best fit to the experimental data and their use is very common in the domain of the adsorption of pesticides in soils.

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