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RESEARCH ARTICLE

ADSORPTION ISOTHERM THE HERBICIDE 2-METHYL-4-CHLOROPHENOXYACETIC ACID IN WATERY PHASE ON SOIL WITH HIGH CONTAINED OF ORGANIC MATTER

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ABSTRACT

Ground and Surface water contamination by herbicides commonly used in rice cultivation is a matter of current concern in Corrientes regions. The fact that most commercial formulations of herbicides containing the active materials in a form immediately available increases the risk of transmission losses of herbicide applied to the crop and, consequently, the risk of contamination of ground and surface water. In this work we presented the adsorption of the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA), widely used to control weeds in the rice cultive on soil high in organic matter (used in rice cultive) from determined from batch test. The adsorption equilibrium data were processed in accordance with four most widely used adsorption isoterms: Freundlich, Langmuir, Temkin and *Dubinin*-Radushkevitch isotherm models. The equilibrium data were best represented by Freundlich isotherm model, showing higher Kd values reveal that adsorption is light.

INTRODUCTION

The strong agricultural character of certain regions of Corrientes and the massive use of pesticides are powerful reasons to carry out careful monitoring of residue levels of pesticides not only surface water but also ground water. Although the latter are more protected from contamination by the natural barrier of the soil and the unsaturated zone, it is not necessary to reject much less his possible pollution, especially for herbicides and polar insecticides highly mobile in soils. Compounds like the phenoxyacetic acid can manage to contaminate the underground waters in aquiferous especially vulnerable. To all of them it is necessary to add his products of transformation, which, in general, are more mobile than the compounds of item. The herbicides of the family of phenoxyacetic acids such as 2-methyl-4-chlorophenoxyacetic acid (MCPA), are hormonal herbicides, that is to say they act in the plant simulating hormones of the growth. Translocated with facility and act systemically in plants and thereby alter the development and growth of the same. They use principally to control the bad grasses dicotyledonous in cultures of grasses and also in woody culture. Although its toxicity is moderate compared to organophosphate pesticides and chlorinated bodies, it is crucial to monitor their waste, especially in water and soil, as they may irreversibly affect the nervous system when adsorbed through the skin and inhalation of the product can cause dizziness and breathing problems (Crespin *et al.*, 2001). The MCPA is readily degraded by soil microorganisms, especially in humid and warm environments, leading to type phenolic metabolites (2-methyl-4-chlorophenol), compounds that are more toxic than phenoxyacid.

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Although this herbicide is used as a salt or ester undergoes hydrolysis processes and soil will be found in its acid form, so that its behavior in soil (solubility, adsorption-desorption, chemical resistance and biodegradation) will be determined by said chemical structure. The MCPA containing a carboxylic group will be the primary responsibility for its relatively high activity (Bolan & Baskaran, 1996; Socías–Viciana *et al.*, 1999; Jensen *et al.*, 2004; Tunega *et al.*, 2004; Agnieszka *et al.*, 2013). On the other hand, contains a lipophilic phenolic structure and therefore MCPA becomes a model substance for study adsorption-desorption processes may experience soils both polar and hydrophobic interactions. The calculation of different parameters of the adsorption process is a good tool for quantitative prediction of the latter. In some cases, for example when the balance is one adsorbate into contact with a solid, the calculations are relatively easy and straightforward. In others, as for example, are present in more than one adsorbate solution or due to other factors such as bacterial growth, calculations can only be carried out by using mathematical models and assumptions. In the case of adsorption of a single adsorbate from a liquid phase onto an adsorbent, is considered constant solvent activity, so that its influence can be ignored. Actually, adsorption of a liquid phase on a solid is a very complex phenomenon. Considerations such as the differences in the orientation of the adsorbed molecules, including formation of micelles or the presence of solvent molecules, can affect the calculations, but often, in order to simplify, is not taken into account (Umpleby *et al*., 2001). During the last two decades, many investigators have proposed a number of models to quantify adsorption processes, establishing various expressions relating the adsorption capacity of the adsorbent (q), given by the expression (1), with the equilibrium concentration (Ce), and it will be remembered is expressed:

$$q_e = \frac{C_i - C_e}{m} \cdot V \qquad (1)$$

Where: q is the value of adsorption; C_i is the initial concentration of adsorbate; C_e is the final concentration; V is the volume of the solution; m is the mass of adsorbent. Adsorption processes have great influence in the behavior and final destination of the pesticides in the environment. Due to, precisely, to that the knowledge of these phenomena is a fundamental tool for the studies of movement of pesticides in the soil, there have been realized a few experiences destined for the obtaining of the coefficients of adsorption of the herbicide MCPA in samples of soils by high place contained of organic matter, of the zone of culture of rice.

EXPERIMENTAL

Preparation of soil

The soils used in the study come from the site near the rice planting area 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 siltloam 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 one preserves them to 4°C up to his analysis. Before the experience the samples dry off and pass for a sieve to retain soil particles less than 2 mm

Herbicide MCPA

2-methyl-4-chlorophenoxyacetic acid (MCPA) CAS N 94-74-6 supplied by Sigma–Aldrich was used as an adsorbate. Deionized water was used to prepare all the solutions and reagents. Solution of MCPA of 1200 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 MCPA compounds were added to 1g portions of the soil in 125 mL flasks. MCPA concentrations ranged from 60.0 to 1080.0 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 MCPA compound was determined in the supernatant by HPLC method.

Equilibrium models

Freundlich isotherm

For simplicity and better interpretation of the phenomenon of adsorption isotherms are the Langmuir and Freundlich have been applied more often. The Freundlich isotherm (Febrianto *et al*, 2009) is an empirical model that assumes that there is no saturation of the adsorbent and hence there is no limit for C_e, is given by the following expression:

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

where Ce 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_d (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. This equation can be linearized by taking logarithms:

$$\ln q_e = \ln K_d + \frac{1}{n} \ln C_e \qquad (3)$$

Thus, the expression (3) represents a straight line whose intersection with the ordinate axis (ln K_d) expresses the adsorptive capacity of the adsorbent and the slope (1/n) measures the intensity of adsorption.

Langmuir isotherm

The Langmuir isotherm (8) is set to the expression:

$$q_e = \frac{q_m C_e}{K_L + C_e} \qquad (4)$$

Where Ce is the equilibrium concentration (mg/L); q_e is the amount MCPA 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). This equation describes a rectangular hyperbola, which passes through the origin and tends to a maximum adsorption (q_m). Its linearization can be done by taking the following expression:

$$\frac{C_e}{q_m} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \qquad (5)$$

Therefore, representing C_e/q_e versus C_e, a straight line is obtained by the value of q_m give the corresponding value of the slope, intercept give the value of the constant K_L. Langmuir model assumes that:

- The adsorbent surface is a series of free active adsorption centers.
- Activity adsorption centers is equal and independent of the presence of other neighboring centers adsorbates.
- A reacts only with adsorbate adsorption center.
- The adsorption is limited to a single layer.

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:

$$q_e = B\ ln\, A + B\ ln\, C_e \qquad (6)$$

where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol); 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).

Dubinin-Radushkevich isotherm

Another model that can be used to fit the experimental data of adsorption from solutions is the model DR (Dubinin-Radushkevich), whose expression is:

$$ln q_e = ln q_m - \beta \cdot E^2 \qquad (7)$$

And

$$E = R \cdot T \cdot ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

Where q_e is the amount adsorbed, q_m represents the amount of solute adsorbed in the monolayer, β is the coefficient for the adsorption energy ($mol^{-1}\ kJ^{-2}$) and E is the potential Polanyi ($kJ\ mol^{-1}$). The parameter β is responsible in principle the surface heterogeneity for each adsorbate-adsorbent system.

RESULTS AND DISCUSSION

Determination of equilibrium parameters

Due to the fact that the process of adsorption is exothermic, a variation of the temperature can lead to a variation in the performance of the process, for what, operate to a constant temperature is a basic requirement for the production of the isotherms of adsorption, in this work the temperature was kept to 25°C. It is important to mention that to choose the appropriate model, it is necessary to give a special care to which the system is situated really in thermodynamic equilibrium. In opposite case, the obtained results can be influenced by other parameters supplementary, such as the accessibility to the binding sites, which generally are translated in an underestimation of the actual capacity of the soil parameters. For his simplicity and the best interpretation of the phenomenon of adsorption, the isotherms of Freundlich and Langmuir are those that have been applied by more frequency, nevertheless in this paper the application of the Temkin isotherm and Dubinin-Radushkevich are tested. The isotherm form and more concretely the initial slope of the curve, contributes information about the mechanism of adsorption, since it depends on the affinity of the adsorbate for the active available centers in the adsorbent. Adsorption studies were carried out, by means of experiments named in batch (for lots), which were based on the agitation of an aqueous solution containing the herbicide, with a certain quantity of soil. After some time, during which it is assumed the equilibrium is reached, the concentration of the herbicide in the supernatant was determined, considering that the difference between the latter and the initial concentration is the amount of adsorbed pesticide on the soil. Equilibrium parameters of the models tested by minimizing the difference between the amount of pesticide absorbed experimentally and calculated according to the model, using Microsoft Excel Solver also determined.

Determination of equilibrium models

The results of adsorption experiments were analyzed by linear regression to the Langmuir model (Figure 1).

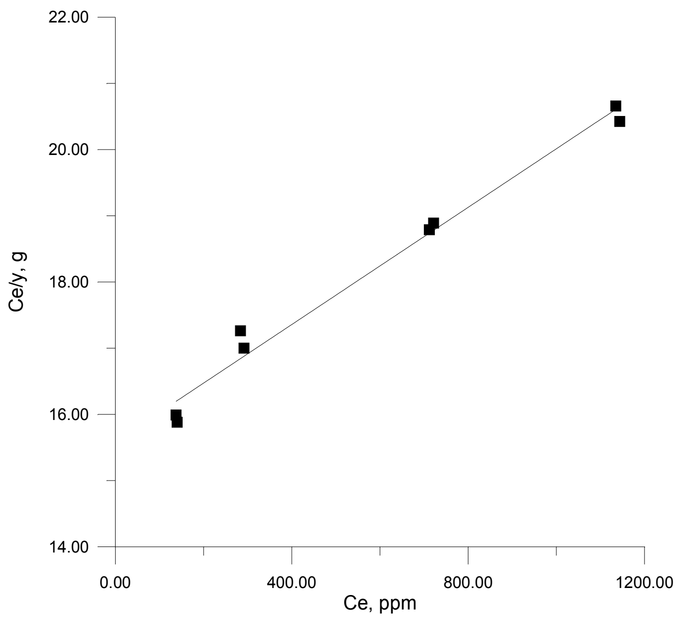

Figure 1. Isotherm model the Langmuir

The constants obtained and the correlation coefficient of the mathematical model of the Langmuir adsorption isotherm is presented in Table 1. The Freundlich isotherm model shown in Figure 2, by adjusting the linear correlation experimental data, obtaining a value of 0.997. Kd and n values are shown in Table 1 are empirical constants of Freundlich that relate to the adsorption capacity and adsorption strength. The value of n for the studied soil is greater than 1 so that according to this model, the adsorption of MCPA is not favorable to the pH value of 6.8, exhibit a low removal of MCPA in the investigated soil. From the results of the thermodynamic analysis according to the Dubinin-Radushkevich model, we obtain the maximum adsorption capacity q_m is 34 ppm/g affinity coefficient β is 4.06 x 10^{-3} (Figure 3, Table 1). A coefficient value as low conditional on dilute solutions. The experimentally obtained data were also analyzed using a linear model of Temkin, and noting Figure 4 along with the data in Table 1, it can confirm a very good correlation of the graphs of isotherm presented.

Table 1. Parameters and correlation coefficients obtained for different models of adsorption isotherm

Isotherm models	Freundlich			Langmuir			Dubinin-Radushkevich			Temkin		
parameters	K_d $(L/g)^{1/n}$	n	R^2	q_m (ppm/g)	K_L x 10^{-4} $(ppm)^{-1}$	R^2	q_m (ppm/g)	β x 10^{-3}	R^2	A (L/g)	B (J/mol)	R^2
Soil	0.163	1.21	0.997	175.89	3.96	0.966	40.00	4.06	0.962	27.62	17.92	0.960

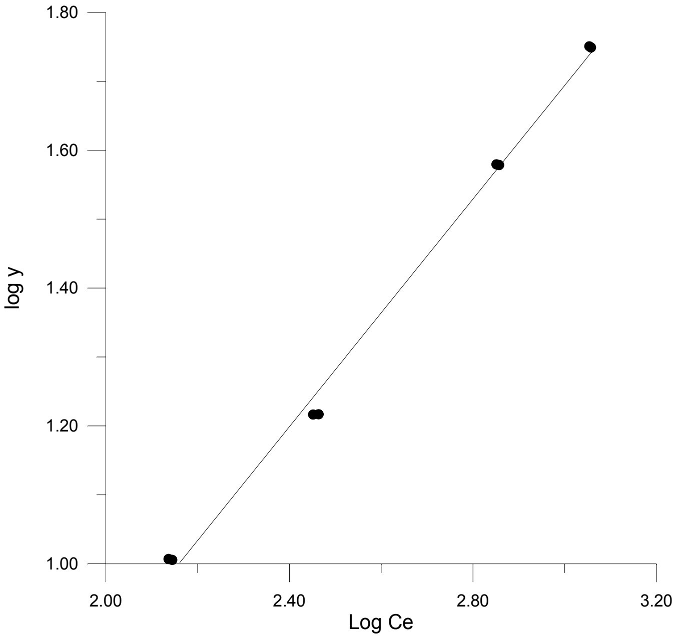

Figure 2. Isotherm model the Freundlich

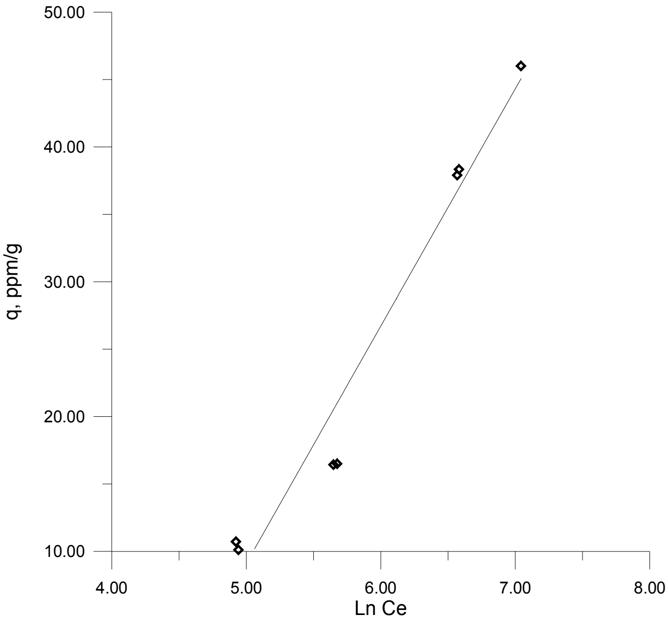

Figure 4. Isotherm model the Temkin

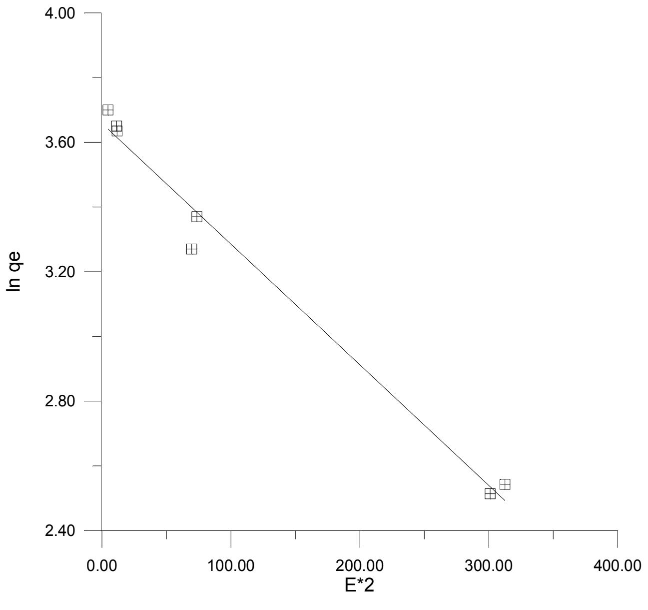

Figure 3. Isotherm model the Dubinin-Radushkevich

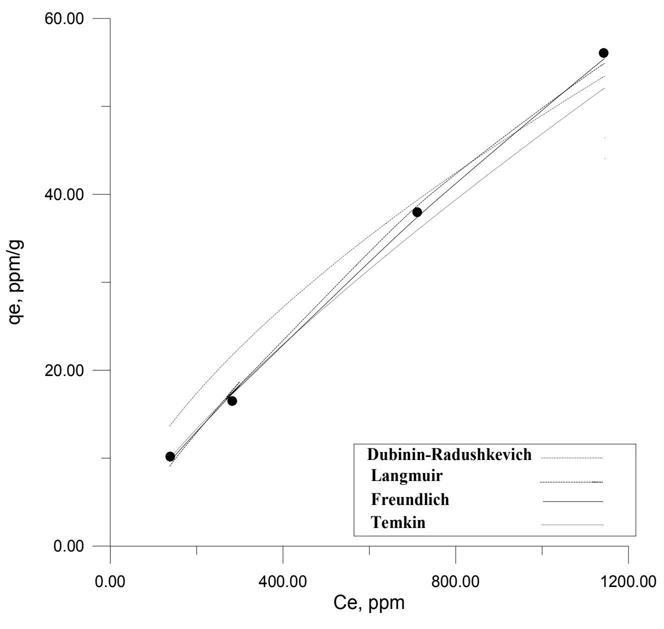

Figure 5. Different models MCPA adsorption isotherm in soil

It can be seen that there is good correlation coefficients (R2) with the coefficients of the models Langmuir, Freundlich and Dubinin-Radushkevich, we can confirm that the Temkin model is a model that can be employed in the analysis of the adsorption of MCPA in soil. The results obtained in the Table 1 indicate us, that though the different models present good coefficients of correlation, the best which adjusts to the experimental information is the model of Freundlich. Figure 5 shows the settings of the various models to the experimental data.

Conclusion

The experimental results were analyzed with the adsorption isotherm models of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin, finding that all the models have a very good performance in their correlation factor (R^2). The adsorption phenomenon described by the Freundlich isotherm obtained in the operation type of the experimental data. In the studied pH (6.8) value of Freundlich constant n gives a higher than 1, but not enough so that the soil will adsorb, indicating that passes easily to polluting groundwater

REFERENCES

Agnieszka, A., Piwowarczyk, N., Holden, M., 2013. Phenoxyalkanoic acid herbicide sorption and the effect of co-application in a Haplic Cambisol with contrasting management. Chemosphere, 90(2): 535-541

Bolan, N.S., Baskaran, S., 1996. Biodegradation of 2,4-d herbicide as affected by its adsorption–desorption behavior and microbial activity of soils. *Aust. J. Soil Res*., 34: 1041-1053.

Crespín, M.A., Gallego, M., Valcárcel, M., 2001. Study of the degradation of the herbicides 2,4-D and MCPA at different depths in contaminated agricultural soil. *Environ. Sci. Technol*., 35: 4265-4270.

Febrianto, J., Kosasih, A.N., Sunar-so, Y., Ju Yi-Hsu, Indraswati, N., Ismadji Sur-yadi, 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *J. Hazard. Mater*. 162(2-3): 616-645.

Jensen, P.H., Hansen, H.C.B., Rasmussen, J., Jacobsen, OS. 2004. Sorption-controlled degradation kinetics of MCPA in soil. *Environ. Sci. Technol.* 38:6662–6668.

Socías–Viciana, M.M., Fernández–Pérez, M., Villafranca–Sánchez, M., González–Pradas, E., Flores–Céspedes, F., 1999. Sorption and leaching of atrazine and MCPA in natural and peat–amended calcareous soils from Spain. *Journal of Agricultural and Food Chemistry*, 47/ 1236–1241.

Tunega, D., Haberhauer, G., Gerzabek, M.H., Lischka, H., 2004. Sorption of phenoxyacetic acid herbicides on the kaolinite mineral surface – an ab initio molecular dynamics simulation. *Soil Sci.,* 169: 44-54.

Umpleby, R.J., Sarah, I., C. Baxter, Chen, Y., Shah, N., Shimizu, K.D., 2001. Characterization of Molecularly Imprinted Polymers with the Langmuir−Freundlich Isotherm. *Anal. Chem*. 73: 4584-4591.

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