



Behavior of 2-methyl-4-chloro-phenoxyacetic acid in rice cultivation soils of the Province of Corrientes, Argentina

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Abstract The herbicide 2-methyl-4-chloro phenoxyacetic acid (MCPA) is widely used in rice crops in different areas of the province of Corrientes. Determining the adsorption kinetics of MCPA, which is the rate of adsorption of a contaminant on the active surface (sorber), which has the same shape as any chemical process or reaction kinetics will allow us to address its transport effects and its persistence in the growing area. The objective of this work was to carry out the adsorption kinetics of MCPA on a rice crop soil, as a function of time, and to determine the influence of temperature on it by the pseudo-first and pseudo-second order models. Both models assume that the main force responsible for adsorption is the difference in adsorbate concentrations that exist between the solution and the surface of the adsorbent. The soils used in the study come from the site near the Mercedes rice planting area and is an Argiacuol. The samples were collected in the winter of 2016 at different depths to differentiate the horizons affected by the work of the soil or for the installation of a permanent cover of vegetables used in direct seeding technique. We work with samples 0-8 cm deep. In general, the soil used in the study are brown in color (Munsell system), hydromorphic silty loam texture, 22% clay, 46% silt and 32% sand, the most important thing is the high content of organic matter (OM). The adsorbate used in this study is MCPA from Sigma-Aldrich; solutions were prepared using deionized water at three temperatures 25 ° C, 35 ° C and 45 ° C. The kinetic studies were carried out following the equilibrium technique in batch for 24 hours. A 1g soil sample was contacted with 30 mL of a 1 mg L⁻¹ MCPA solution in CaCl₂ and a follow-up was carried out taking data at 1-hour intervals during the 24 h. The adsorption capacity (q_e) of MCPA was determined by the correlation: $q_e = V (C_i - C_e) / m$, where C_i is the initial concentration of MCPA (mg L⁻¹), C_e is its concentration at equilibrium (mg L⁻¹), V is the volume of solution in liters, m is the mass of adsorbent expressed in grams and q_e is the adsorption capacity (mg g⁻¹). The remaining MCPA concentration was determined by HPLC. It was observed that the experimental kinetic data have a higher correlation with the pseudo-second order model. Intraparticle diffusion was also studied to see if this is the rate-limiting mechanism.

Keywords kinetic, sorption, herbicide, models, degradation, diffusion, isotherm

Introduction

Pesticides applied to crops enter the soil by dispersal of the product, runoff or the incorporation of contaminated crop residues. Once present in the soil, pesticides migrate from one compartment to another and act as a source of

contamination to air, surface and groundwater. The use of pesticides has several drawbacks since they alter the balance of nature, unbalancing ecological systems [1]. The magnitude of the hazard depends on its residence time in the soil [2-4]. The residues of these compounds can reach areas further away from the application area, carried by the wind, continental water, marine currents and through biological chains [5].

Adsorption is the most important mechanism for directly or indirectly influencing the magnitude and effect of the other mechanisms and is a phenomenon of attraction between a solid surface and a liquid or a vapor, the pesticide molecules can be adsorbed or retained by colloids present in the soil, clay and organic matter, during the leaching process [6,7].

The influence of temperature on the adsorption kinetics of pesticides as well as obtaining the kinetic parameters and their adjustment to mathematical models is of interest. The methodology and results obtained here can be used to predict the behavior of adsorption processes under different environmental conditions.

2. Material and Methods

2.1. Soil

The soil samples used in the study belong to the town of Mercedes in the province of Corrientes. The sample corresponds to the surface layer (0-8 cm) of a soil dedicated to rice cultivation. The texture of the topsoil was brown clay silty loam (Munsell system) with the following particle contents: 22% clay, 46% silt and 32% sand, with average organic carbon (OC) content 1.61%; pH 5.8; CEC 12.5 cmol kg⁻¹, Ca²⁺ 7.7 cmol kg⁻¹. Its characteristics were determined by the usual methods of soil analysis [7]. The samples were dried, ground and sieved through a 2 mm mesh and stored at 4 °C until their subsequent analysis.

2.2. Herbicide analysis

MCPA was quantified in 1 mL of the fraction extracted from the solution in equilibrium with the soil by solid phase extraction (SPE), using high performance liquid chromatography (HPLC). An Agilent 1120 compact LC chromatograph was used. The separation was carried out on an ODS Eclipse plus column (14 x 4 mm id, 5 µm particle size) with a mobile phase consisting of 35:65 acetonitrile: methanol / water with 0.1% orthophosphoric acid. The mobile phase flow of 1.2 mL min⁻¹ and an injection volume of 20 µL. Under these conditions, the MCPA retention time was 2.9 min.

2.3. Adsorption kinetics

The kinetic experiments have been carried out following the "batch" technique proposed by Guide No. 106 for the control of chemicals, of the Organization for Economic Development (OECD, 2000) [8]. It was carried out at 25, 35 and 45°C.

In each experiment, 30 mL of pesticide solution of 1 mg L⁻¹ of MCPA were put in contact with 1 g of soil and stirred in a rotary shaker and at constant temperature. After shaking, the solution was centrifuged at 5000 rpm for 10 minutes. The supernatant was used for the extraction of MCPA by SPE and was analyzed by HPLC. The concentrations of MCPA in solution was determined at different intervals of time: after 1 hour of stirring and contact, and every hour until 24 hours. All the experiments were carried out in triplicate.

3. Results and Discussion

3.1. Effect of Contact Time

The effect of the stirring or contact time between the solid-liquid phases in an adsorption process is an important factor that influences the characteristics of these processes, since they determine the equilibrium distribution of the adsorbate and adsorbent, establishing the equilibrium time and describing its kinetics. There is a large number of kinetic models reported in the specialized literature, however the most tested kinetic models in these systems are those of pseudo first order, pseudo second order, Elovich and intraparticle diffusion.

In general, the adsorption capacity of MCPA in soil can be calculated through the principle of mass transfer according to equation (1).



$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where q_t is the amount of MCPA adsorbed at equilibrium (mg g^{-1}), C_0 and C_t (mg L^{-1}) are the concentrations initial and at time t in the liquid phase of the MCPA, V is the volume of solution (L) and m is the mass of adsorbent (g).

3.2. Modeling of Adsorption Kinetics

According to Weber and Smith (1987) [9] the transfer of a compound from a liquid phase to an adsorption site is carried out in four stages: the transfer of the compound from the liquid to the film near the solid adsorbent (fast stage), the transfer of the compound through the liquid film near the outer surface of the adsorbent (external mass transfer), diffusion of the compound into the adsorbent particle (intraparticle diffusion), and adsorption itself, which is a rapid step. The adsorption kinetics is determined by the slowest stage, that is, external mass transfer (K_f) and intragranular surface (D_s) and / or porous (D_p) diffusion. However, for most of the authors, the effect of surface diffusion is greater when compared to porous diffusion. Komiyama and Smith (1974) estimate that the effect of surface diffusion is twenty times more important than the effect of porous diffusion [11]. Therefore, porous diffusion will not be considered in this work.

The data obtained in the kinetic study have been adjusted to 4 kinetic models.

3.2.1 Pseudo first order model

The pseudo first order kinetic model (PPOR) is mainly based on the adsorption capacity of the adsorbent and the determination of the speed of the adsorption process. This is commonly used for homogeneous systems that propose a physical adsorption process, described by the Lagergren equation [10], the linear form of this model is presented in equation (2), where q_e and q_t (mg g^{-1}) are the amount of MCPA adsorbed on the adsorbent at equilibrium and at time t , and k_1 (min^{-1}) is the pseudo-first order rate constant. Figure 1

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

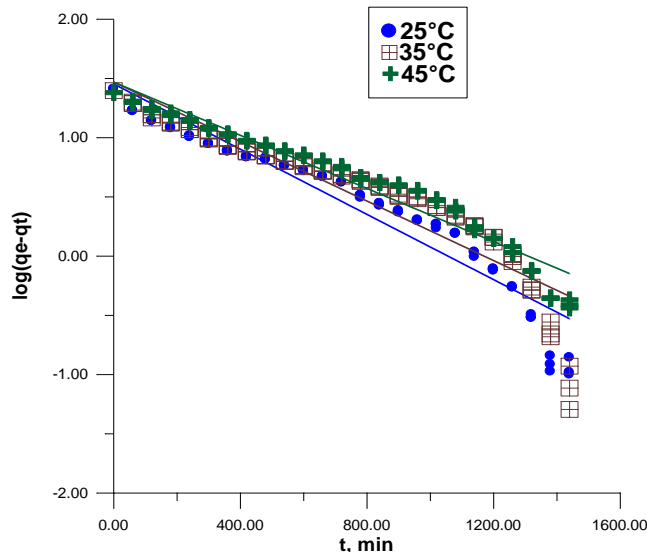


Figure 1: Pseudo first order model

In this model, the variation in the adsorption rate should be proportional to the concentration at the first order for a strictly superficial adsorption. If there is no linearity in this model, it is added to the limiting of the diffusion between pores.

From the slope and the intercept, the values of k_1 can be deduced and the experimental values of q_e can be corroborated against the theoretical ones; if there is a large discrepancy between these values, the pseudo first order kinetics does not describe this system.

3.2.2. Pseudo second order model

The pseudo second order model (PSOR) assumes a chemical adsorption process, attributed to the distribution of the valence forces or electron exchange between adsorbate and adsorbent, therefore, assigning an effective adsorption capacity, which is proportional to the number of active sites occupied in the adsorbent [11]. Its linear equation (Eq. (3)) is shown below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where q_e and q_t (mg g^{-1}) are the amount of MCPA adsorbed on the adsorbent at equilibrium and at time t , and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant. Therefore, in order to deduce the constants of the second order kinetics, it is necessary to make a graph of (t / q_t) vs. (t) , from which a straight line should be obtained and from its slope and intercept, the theoretical equilibrium concentration and the constant of the equation can be obtained, respectively; the theoretical q_e value is compared with the experimental one of the measurements, if the values are very close, the model obeys the pseudo second order model. It can be seen that the kinetics of MCPA adsorption in Arguiguel follows this model with correlation coefficients greater than 0.990. These results imply that the chemisorption mechanism plays an important role for the adsorption of MCPA.

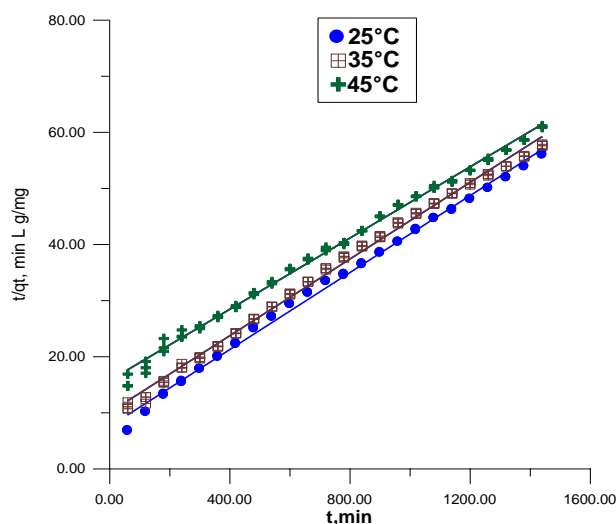


Figure 2: Pseudo second order model

3.2.3. Elovich model

The Elovich kinetic model (ME) is applied to heterogeneous solid-liquid adsorption systems, this model is suitable for general applications that have chemisorption kinetics and covers a wide range of slow adsorption, its linear equation (4) is described below [12]:

$$q_t = \beta \ln \alpha \beta + \beta \ln t \quad (4)$$

Where q_t ($\text{mgL}^{-1} \text{g}^{-1}$) is the amount of MCPA adsorbed on the adsorbent at time t , β is the equilibrium adsorption constant ($\text{mgL}^{-1} \text{g}^{-1} \text{min}^{-1}$) and α is related to the surface area covered and the chemisorption activation energy (L g mg^{-1}). Figure 3



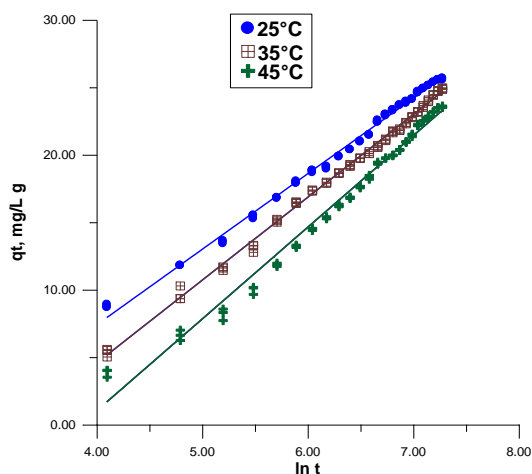


Figure 3: Elovich model

The data obtained from the kinetic experiments are observed in Figure 3 and the parameters obtained in Table 1. From Table 1 a good correlation is observed between the experimental points and the theoretical lines. This implies that Elovich's model describes the kinetic data well over a short period of time. When the correlation between the sorption capacity and the constant β is negative, it is accepted that the adsorbent does not retain the adsorbate. The positive value of the constants gives evidence that adsorption occurs. The value of R^2 were 0.9953, 0.9971 and 0.9856, and they are in agreement with the results of the Pseudo-second-order model. The applicability of the simple Elovich equation to current kinetic data indicates that the Elovich equation was able to adequately describe the initial kinetics of MCPA sorption on the surface of Argiguol.

3.2.4. Modelo de Difusión intrapartícula

The intraparticle diffusion method (IPM) is a multi-stage process that involves the transport of solute molecules from the aqueous phase to the surface of the solid particles and subsequently the diffusion of the solute molecules into the pores. Thereby which is likely to be a slow process based on the speed theory proposed by Webber and Morris [13] and its linear equation is show below in equation (5):

$$q_t = k_p t^{1/2} + C_i \quad (5)$$

Where q_t ($\text{mg L}^{-1} \text{g}^{-1}$) is the amount of MCPA adsorbed on the adsorbent at time t , k_p is the speed parameter of stage i ($\text{mg L}^{-1} \text{g}^{-1} \text{min}^{-1/2}$), calculated from the slope of the straight line of q_t vs $t^{1/2}$. C_i is the interparticle diffusion coefficient ($\text{mg L}^{-1} \text{g}^{-1}$). Figure 4

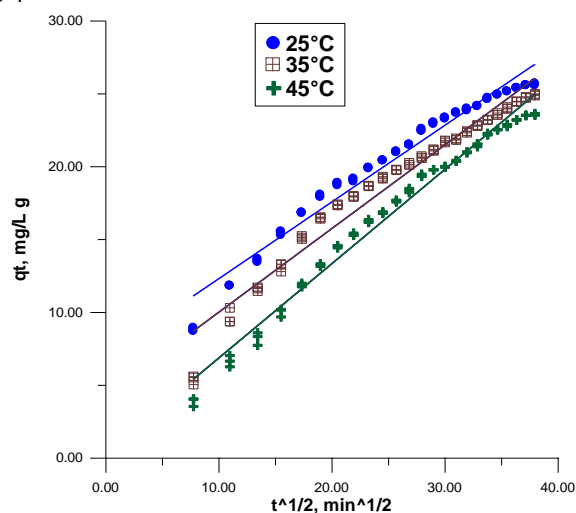


Figure 4: Intraparticle Diffusion Model

The structure of the soil and its interaction with the diffusion of the substance influences the speed of transport. A high k_p value illustrates improved adsorbate-adsorbent particle binding, it may simply be due to the higher adsorbate concentration that induces higher diffusion forces of the adsorbate molecules in the pores.

The correlation coefficients (R^2) for the intraparticle diffusion model were 0.9686, 0.9594 and 0.9829 for 25, 35 and 45°C, respectively (Table 1). These relatively low R^2 values compared to PSOR and ME suggest that intraparticle diffusion may not be the only rate limiting step in the procedure. According to Itodo *et al.* [14], the adsorption mechanism involves intraparticle diffusion if the following conditions are met: (a) high R^2 values to determine applicability; (b) straight line through the origin for the plotted area qt versus $t^{1/2}$. (c) Intercept $C_i < 0$. A validity test that deviates from (b) and (c) above shows that the mode of transport is affected by more than one process, which means that two or more stages occur. It is evident that the straight lines did not pass through the origin, that is, $C_i > 0$ for all cases, further indicating that intraparticle diffusion is not the only stage of speed control.

Table 1: Parameters that describe the kinetic models

Models		PPOR			PSOR		
Temperature °C	q_e ($\text{mg L}^{-1}\text{g}^{-1}$)	$k_1 10^3$ (min^{-1})	R^2	q_e ($\text{mg L}^{-1}\text{g}^{-1}$)	$k_2 10^4$ ($\text{g L mg}^{-1}\text{min}^{-1}$)	R^2	
25	4.27	1.4	0.9145	29.15	1.57	0.9957	
35	4.34	1.3	0.8516	29.32	1.16	0.9962	
45	4.33	1.1	0.9461	31.54	0.64	0.9960	
Models		ME			MIP		
Temperature °C	α (g mg^{-1})	β ($\text{mg g}^{-1}\text{min}^{-1}$)	R^2	k_p ($\text{g g}^{-1}\text{min}^{-1/2}$)	C_i (g g^{-1})	R^2	
25	0.012	5.59	0.9953	0.53	7.02	0.9686	
35	0.006	6.14	0.9971	0.57	4.24	0.9594	
45	0.003	6.80	0.9856	0.65	0.37	0.9829	

4. Conclusions

The equilibrium and kinetic isothermal model values suggest that MCPA is strongly adsorbed in the soil. The soil showed a rapid sorption of MCPA and a theoretical sorption capacity of approximately 1.3 g MCPA / g sorbent. A comparison of the results of the regression coefficients R^2 in Table 1 shows that the adsorption process is mainly monolayer and the form of adsorption is by chemisorption. The relatively low R^2 values of the MIP model also suggested that intraparticle diffusivity may not have been the only rate-limiting step in the sorption procedure. The results showed that MCPA sorption by soil is feasible, suggesting that it does not contaminate groundwater.

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Competing interests

Authors have declared that no competing interests exist.

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