

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

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## ABSTRACT

**Aim:** This study was aimed 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.

**Method and Materials:** 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. Samples were 0-8 cm deep and the soil used in the study were brown in color (Munsell system), hydromorphic silty loam texture, 22% clay, 46% silt and 32% sand, the most important thing was high content of organic matter (OM). The adsorbate used in this study was MCPA from Sigma-Aldrich; solutions were prepared using deionized water at three temperatures 25 °C, 35 °C and 45 °C.

**Results:** 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<sup>-1</sup> MCPA solution in CaCl<sub>2</sub> and a follow-up was carried out taking data at 1-hour intervals during the 24 h. The adsorption capacity (q<sub>e</sub>) of MCPA was determined by the correlation:  $q_e = V (C_i - C_e) / m$ , where C<sub>i</sub> was initial concentration of MCPA (mg L<sup>-1</sup>), C<sub>e</sub> was its concentration at equilibrium (mg L<sup>-1</sup>), V was volume of solution in liters, m was mass of adsorbent expressed in grams and q<sub>e</sub> was adsorption capacity (mg g<sup>-1</sup>). The remaining MCPA concentration was determined by HPLC.

**Conclusion:** It was concluded 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.

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## 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 it alters the balance of nature, unbalancing ecological systems (Primo and Carrasco, 1997). The magnitude of hazard depends on its residence time in the soil (El Bakouri et al., 2009 and 2010). 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 (Badii and Landeros, 2007). 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 (Beltrán et al., 1995 and Uzunova et al., 2013).

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.

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## Materials and Methods

**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<sup>-1</sup>, Ca<sup>2+</sup> 7.7 cmol kg<sup>-1</sup>. Its characteristics were determined by the usual methods of soil analysis<sup>7</sup>. The samples were dried, ground and sieved through a 2 mm mesh and stored at 4 °C until their subsequent analysis.

**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<sup>-1</sup> and an injection volume of 20 µL. Under these conditions, the MCPA retention time was 2.9 min.

**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). It was carried out at 25, 35 and 45°C.

In each experiment, 30 mL of pesticide solution of 1 mg L<sup>-1</sup> 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.

## Results and Discussion

### *Effect of contact time*

The effect of the stirring or contact time between the solid-liquid phases in an adsorption process was 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. Large number of kinetic models was reported in the specialized literature, however the most tested kinetic models in these systems were 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  $q_t$  was the amount of MCPA adsorbed at equilibrium (mg g<sup>-1</sup>),  $C_0$  and  $C_t$  (mg L<sup>-1</sup>) were the concentrations initial and at time  $t$  in the liquid phase of the MCPA,  $V$  is the volume of solution (L) and  $m$  was the mass of adsorbent (g).

### *Modeling of Adsorption Kinetics*

According to Weber and Smith (1987) the transfer of a compound from a liquid phase to an adsorption site was 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 was a rapid step. The adsorption kinetics was determined by the slowest stage that was 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 was greater when compared to porous diffusion. Komiyama and Smith (1974) estimated that the effect of surface diffusion was twenty times more important than the effect of porous diffusion (Ho and McKay, 1999). Therefore, porous diffusion could not be considered in this work.

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

### *Pseudo first order model*

The pseudo first order kinetic model (PPOR) was mainly based on the adsorption capacity of the adsorbent and the determination of the speed of the adsorption process. It was commonly used for homogeneous systems that propose a physical adsorption process, described by the Lagergren equation (Ho, 2004), the linear form of the model was presented in equation (2), where  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) were the amount of MCPA adsorbed on the

adsorbent at equilibrium and at time  $t$  and  $k_1$  ( $\text{min}^{-1}$ ) was the pseudo-first order rate constant (Fig. 1)

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

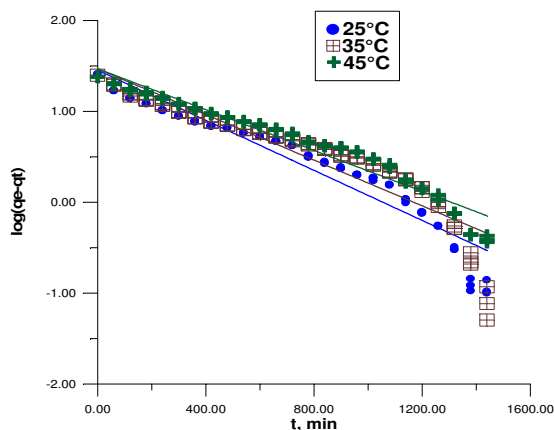


Fig. 1. Pseudo first order model

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.

#### 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 was proportional to the number of active sites occupied in the adsorbent (Ho and McKay, 1999). Its linear equation (Eq. (3)) was shown below:

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

Where  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) were the amount of MCPA adsorbed on the adsorbent at equilibrium and at time  $t$ , and  $k_2$  ( $\text{gmg}^{-1}\text{min}^{-1}$ ) was the rate constant. Therefore, in order to deduce the constants of the second order kinetics, it was 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

was 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 Arguigoul 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.

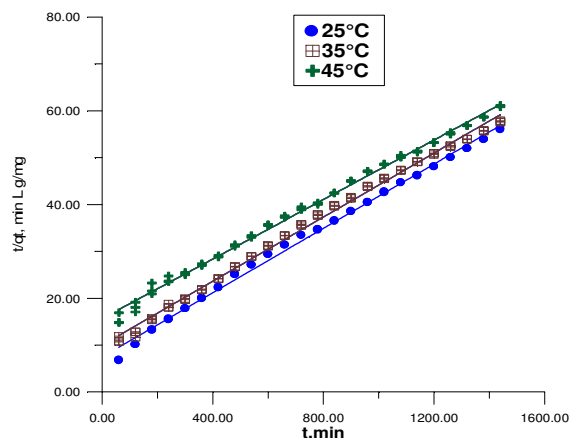


Fig. 2. Pseudo second order model

#### Elovich model

The Elovich kinetic model (ME) was 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) was described below (Wua et al., 2009):

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

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

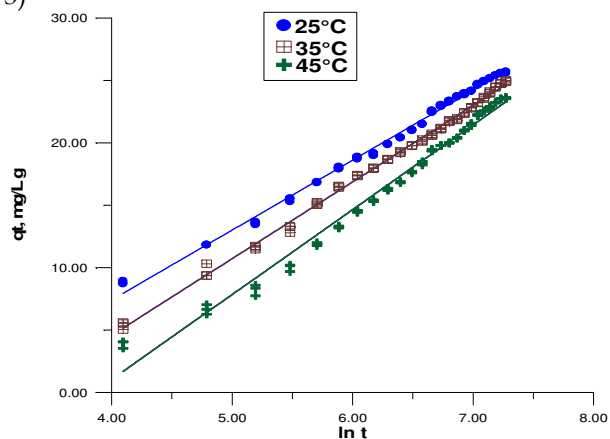


Fig. 3. Elovich model

Table 1. Parameters that describe the kinetic models

Models	PPOR			PSOR		
	$q_e$ ( $\text{mg L}^{-1}\text{g}^{-1}$ )	$k_1 10^3$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ ( $\text{mg L}^{-1}\text{g}^{-1}$ )	$k_2 10^4$ ( $\text{g L mg}^{-1}\text{min}^{-1}$ )	$R^2$
Temperature $^{\circ}\text{C}$						
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 $^{\circ}\text{C}$	$\alpha$ ( $\text{g mg}^{-1}$ )	$\beta$ ( $\text{mg g}^{-1}\text{min}^{-1}$ )	$R^2$	$k_p$ ( $\text{g g}^{-1}\text{min}^{-1/2}$ )	$C_i$ ( $\text{g g}^{-1}$ )	$R^2$
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

The data obtained from the kinetic experiments were observed in Figure 3 and the parameters obtained (Table 1). A good correlation was observed between the experimental points and the theoretical lines. This implied 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  $\beta$  was negative, it was accepted that the adsorbent does not retain the adsorbate. The positive value of the constants gave evidence that adsorption occurs. The value of  $R^2$  was 0.9953, 0.9971 and 0.9856, and they were in agreement with the results of the Pseudo-second-order model. The applicability of the simple Elovich equation to current kinetic data indicated that the Elovich equation was able to adequately describe the initial kinetics of MCPA sorption on the surface of Argiguol.

#### Model of intraparticle Diffusion

The intraparticle diffusion method (IPM) was a multi-stage process that involved 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 was likely to be a slow process based on the speed theory proposed by Webber and Morris (1963) and its linear equation is show below in equation (5):

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

Where  $q_t$  ( $\text{mg L}^{-1}\text{g}^{-1}$ ) was the amount of MCPA adsorbed on the adsorbent at time  $t$ ,  $k_p$  was 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  $q_t$  versus  $t^{1/2}$ .  $C_i$  was the interparticle diffusion coefficient ( $\text{mg L}^{-1}\text{g}^{-1}$ ) (Fig. 4).

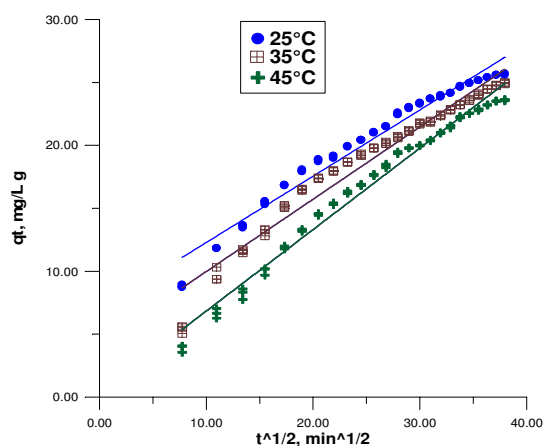


Fig. 4. Intraparticle Diffusion Model

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 $^{\circ}\text{C}$ , 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.* (2010), 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  $q_t$  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 was evident that the straight lines did not pass through the origin that was,  $C_i > 0$  for all cases, further indicating that intraparticle diffusion was not the only stage of speed control.

### Conclusion

It was concluded that equilibrium and kinetic isothermal model values suggested 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  $R^2$  showed that the adsorption process is mainly monolayer and the form of adsorption was 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.

### Reference

- Badii M and Landeros J (2007). Plaguicidas que afectan a la salud humana y la sustentabilidad. *CULCyT/Toxicología de Plaguicidas.*, 19: 21-34.
- Beltrán J, Hernández F and Morell I (1995). Estudios de Adsorción de Plaguicidas en Suelos Mediante Experiencias en Batch. *Avances en la Investigación en Zonas No Saturadas*. Ed. J.M. Gonzalo, I. Antigüedad, 257-268.
- El Bakouri H, Usero J, Morillo J, Rojas R and Ouassini A (2009). Drin pesticides removal from aqueous solutions using acid-treated date stones. *Bioresour. Technol.* 100(10): 2676-2684.
- El Bakouri H, Morillo J, Usero J, Vanderlinden E and Vidal H (2010). Effectiveness of acid-treated agricultural stones used in biopurification systems to avoid pesticide contamination of water resources caused by direct losses: Part I. Equilibrium experiments and kinetics. *Bioresour Technol.*, 101(14): 5084-5091.
- Ho Y-S (2004). Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics.*, 59(1): 171-177
- Ho YS and McKay G (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34(5): 451-465
- Itodo AU, Abdulrahman FW, Hassan LG, Maigandi SA and Itodo HU (2010). Intraparticle Diffusion and Intraparticulate Diffusivities of Herbicide on Derived Activated Carbon. *Researcher*, 2(2): 74-86.
- OECD (2000). OECD guidelines for the testing of Chemicals. Sorption/desorption using a batch equilibrium method OECD Test Guideline, 106. OECD Publications, Paris.
- Primo Yufera E and Carrasco Dorrien JM (1997). *Química Agrícola II Plaguicidas y Fitorreguladores*. Editorial Alambra. Buenos Aires.
- Uzunova S, Uzunov I and Angelova D (2013). Liquid-Phase sorption of oil by carbonized rice husks: impact of grain size distribution on grain size distribution on the sorption kinetics. *J. Chem. Technol. Metall.*, 48(5): 505-512.
- Weber WJ and Morris JC (1963). Kinetics of adsorption on carbon from solutions. *J. Sanit. Eng. Div.* 89: 31-42.
- Weber WJ and Smith JM (1987). Simulation and Design Models for Adsorption Processes. *Environmental Science & Technology*, 21: 1040-1050.
- Wua FC, Tseng RL and Juang RS (2009). Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems *Chemical Engineering Journal*, 150: 366-373

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