Evaluating the Adsorptive Capacity of Aluminoferric Red Oxisol in Reducing the Availability of 2,4-Dichlorofenoxiacetic Acid

D.P. Baldisseralli, D.P. Siqueira, A. Dervanoski, M. Morais, L. Galon, E.P. Korf, G.D.L.P. Vargas

Abstract. Increased food production results in the development and application of agrochemicals to control weeds, which can affect agricultural production. Pesticides contaminate the environment and change soil and water quality. Therefore, to improve the understanding of the adsorption mechanism of 2,4-dichlorophenoxyacetic acid (2,4-D) in aluminoferric red oxisol we have conducted an adsorption study using Langmuir and Freundlich isotherms, treating kinetic data using pseudo first-order, pseudo second-order, and intraparticle diffusion models. The results showed the Freundlich isotherm fits the experimental data best, revealing favorable adsorption and a strong attraction between adsorbent molecules, considering the $n_F$ and $k_F$ model parameters of 3.7 and 34.21 L/g, respectively. The kinetic model with the best fit was the pseudo second-order model. The intraparticle diffusion model indicated the second step as the process controlling step, revealing $k_D$ of 12.36 and 4.42 mg/g for the concentrations of 6352.80 mg/L and 1087.20 mg/L, respectively. Higher $k_D$ represents lower transport resistance and higher motive power for mass transfer.

Keywords: adsorption isotherms, adsorption kinetics, agrochemicals, intraparticle diffusion model, pseudo second-order model.

1. Introduction

Global demand for food has grown considerably in recent decades due to population increase, which has resulted in increased food production. Weeds are prevalent in monoculture agriculture, causing the widespread use of pesticides (Martins et al., 2014). Some farmers adopt a pre-established control system to apply pesticides that do not consider local conditions, such as soil type, climate, agricultural management, type of cultivar, or cropping system (Mancuso et al., 2011). Thus, in soil it is estimated a concentration increase every year and therefore being able to exceed the limits permitted by environmental standards (Cotillas et al., 2018). Consequently, high concentrations have been identified in several environmental compartments and can be spreading easily due the solubility of many pesticides, increasing he extension of the contaminated area (Pavlovic et al., 2005; Piaia et al., 2017).

The southern region of Brazil, more specifically, Rio Grande do Sul state, is known as agricultural, with its main crops being soy, corn and wheat. Among different types of herbicides used in agriculture, stand out the selective ones, such as 2,4-dichlorophenoxyacetic acid, also called 2,4-D, used for post-emergence application on weeds, for various crops such as soybeans and wheat. Its use intended to eliminate the presence of these weeds that may end up compromising production. This herbicide presents short to medium persistence in the soil, being maintained for prolonged periods and can reach up to 4 weeks in regions with tropical characteristic; in cold and dry regions its decomposition becomes very reduced (Silva & Silva, 2007), which can come to affect this ecosystem, as well as, to compromise subsequent plantations, reducing production.

The degradation of agricultural soils by 2,4-D has recently become a concern for researchers (Risco et al., 2016; Souza et al., 2016a). It is commercially distributed in amine formulations, salts, and esters (Amarante Jr. et al., 2003; Shano et al., 2013). Amines were adsorbed more effectively in the soil than those of ester, therefore, more leachable, while those of ester are poorly soluble, therefore they present less movement (Silva & Silva, 2007). The active element of 2,4-D is widely used in the chemical industry, and due to the specific characteristics of this agrochemical, such as high water solubility (620 mg/L) (Pavlovic et al., 2005; Souza et al., 2016b), low biodegradability (Brillas et al., 2003; Nethaji & Sivasamy, 2017), and low soil adsorption coefficient, it is commonly found in groundwater because it percolates through the soil (Prado et al., 2016).

Considered moderately toxic by the World Health Organization (WHO, 2004), this long-lasting herbicide damages the nervous system of living beings (humans and ani-

Duiane Paula Baldisseralli, Undergraduate Student, Universidade Federal da Fronteira Sul, Erechim, RS, Brazil. e-mail: daianebaldisseralli.db@gmail.com.
Diego Pereira Siqueira, M.Sc., Researcher, Universidade Federal de Goiás, Goiânia, GO, Brazil. e-mail: diegooply@gmail.com.
Adriana Dervanoski, Ph.D., Associate Professor, Universidade Federal da Fronteira Sul, Erechim, RS, Brazil. e-mail: dervanos@gmail.com.
Manuela de Morais, M.Sc. Student, Universidade Federal da Fronteira Sul, Erechim, RS, Brazil. e-mail: manuellademorais@gmail.com.
Leandro Galon, Ph.D., Associate Professor, Universidade Federal da Fronteira Sul, Erechim, RS, Brazil. e-mail: leandrogalon@uffs.edu.br.
Eduardo Pavan Korf, Ph.D., Associate Professor, Universidade Federal da Fronteira Sul, Erechim, RS, Brazil. e-mail: eduardokorf@gmail.com.
Gean Delise Leal Pasquali Vargas, Ph.D., Associate Professor, Universidade Federal da Fronteira Sul, Erechim, RS, Brazil. e-mail: geandelise@uffs.edu.br.
Submitted on March 18, 2019; Final Acceptance on August 2, 2019; Discussion open until April 30, 2020.
DOI: 10.28927/SR.423301

Soils and Rocks, São Paulo, 42(3): 301-309, September-December, 2019. 301
mals). Its oral and dermal lethal dose (LD50) is 370 mg/kg (in rabbits) and 1400 mg/kg (in mice), respectively (Vieira et al., 1999). From this perspective, it is important to understand the adsorption mechanisms of pesticides in the soil, as different processes are also affected by this dynamic, such as degradation, bioaccumulation, transport, and mobility (Long et al., 2015).

Adsorption is a multi-step process involving the transport of adsorbate molecules (2,4-D) from the aqueous phase to the surface of the solid (soil) particles, followed by the diffusion of solute molecules into the pore interiors. If the experiment is a batch system with rapid shaking, there is a possibility that the transport of adsorbate from the solution into pores (bulk) is the step that controls the speed of the process (McKay, 1982). This process is described by a graphical relationship, that shows the amount of adsorbed 2,4-D varying with the square root of time (Weber & Morris, 1963).

Numerous studies have been conducted to clarify the behavior and adsorption of herbicides, such as terbutylazine, prometryne, metribuzin, hexazinone, metolachlor, chlorotoluron, trifluralin, azoxystrobin, fipronil, chlorimuron-ethyl, chlorimuron, atrazine (Yue et al., 2017), in soil. Regarding 2,4-D, research has demonstrated that in soils with a higher amount of organic matter, whether natural or derived from residues, the adsorption of pesticides by soil particles is higher (Amarante Jr. et al., 2003; Bekbőlet et al., 1999; Spadotto et al., 2003; Vieira et al., 1999; Rodriguez-Rubio et al., 2006).

Although 2,4-D is classified as an extremely toxic product in Brazil, its use is permitted and therefore there are many concerns about the effects on human health and the environment. Therefore, knowledge is essential about the mechanisms of retention and mobility of this contaminant in the soil. There have been numerous studies about the adsorption of this pesticide in Brazilian soil, however, there is a lack of research on the use of latosol with low organic matter as adsorbent material. To increase knowledge about the capacity and mechanisms of the adsorption of the 2,4-D agrotoxic in aluminoferric red oxisol (Erechim unit) (Streck et al., 2008).

Samples were taken from the surficial layer of horizon A soil (from 0 to 10 cm) of a site that never received agrochemicals in order to avoid interference from other contaminating sources. Physical and physico-chemical characterization was performed for different attributes, such as: pH, micronutrients (iron, copper, zinc and manganese), soil density and organic matter content; these analyses were performed based on methodology described by Embrapa (2009); and moisture content and granulometric analysis, through the Brazilian Standards NBR 6457 and NBR 7181, respectively (ABNT, 2016; ABNT, 1984).

2.2. Evaluation of adsorption capacity and kinetic study

Under unsteady environment temperature (23 °C ± 1 °C) and pH 5.5, the mass of 2.5 g of soil was added to 50 mL of aqueous solution (1:20), and then, soil adsorption capacity was evaluated using a static method by American Society for Testing and Materials (ASTM, 2016). All the adsorption tests were conducted in triplicate, and the variables evaluated were the concentration of 2,4-D in the liquid phase at equilibrium (C_e), and through mass balance (Eq. 1), the amount of 2,4-D adsorbed on the solid phase (q_e) per unit mass of soil used as adsorbent was obtained.

Initially, a kinetic study was performed in which two initial concentrations of the 2,4-D contaminant (1087.20 and 6352.80 mg/L) were used, resulting from the used volumes of 0.25 and 1.30 liters per hectare, which are extreme values for application of 2,4-D, normally used in the field. These tested volumes are close to those recommended for agronomic application and the purpose of using these concentrations was to obtain the time at which the system reaches equilibrium. Monitoring time was 480 min, however, pre-tests verified that the highest adsorption rates occurred during the first hour of the study. Based on these results, it was determined that in the adsorption kinetic assays the aliquots would be withdrawn at shorter time intervals at the beginning of the kinetic study (5, 15, 30, and 45 min), with the experiment ending after eight hours. This study was used to perform the kinetic modeling of the process, which will be described later. Table 1 shows the experimental conditions used in the preliminary tests and in the kinetic study.

Subsequently, the adsorption study was carried out in triplicate, using initial concentrations of the 2,4-D contaminant of 0.0, 1668.80, 4734.40, 8318.40, 10176.00, and 17920.00 mg/L resulting from 2,4-D applications of 0.0, 0.50, 1.00, 1.50, 2.00, and 3.50 L per hectare of soil used in the field to obtain adsorption isotherm models, with the 2,4-D adsorbate concentration at equilibrium (C_e). Aliquots resulting from the kinetic study and the adsorption study were used to determine the amount of 2,4-D.

2. Methodology

2.1. Solutions and adsorbent

2,4-D pesticide was used in the amine formulation of 720 g/L. The solutions required for the study were prepared with ultrapure water from the Millipore Milli-Q system. The investigated soil was collected in the experimental area on the Erechim campus of the Federal University of Fronteira Sul (UFFS) in Rio Grande do Sul, Brazil. This soil is residual basalt material with a pedological classification of aluminoferric red oxisol (Erechim unit) (Streck et al., 2008).

302 Soils and Rocks, São Paulo, 42(3): 301-309, September-December, 2019.
2.4. Adsorption process modeling

Sites (McKay et al., 1982). The Langmuir isotherm model, presented in Eq. 2, assumes uniform adsorption energy on the surface and in the transmigration of the adsorbate between sites (McKay et al., 1982).

\[ q_e = \frac{q_{max} b_C C_e}{1 + b_C C_e} \]  
(2)

\( q_e \) is the amount of solute adsorbed per unit mass of adsorbent (mg/g), \( C_e \) is the adsorbate concentration at equilibrium (mg/L), and \( q_{max} \), (mg/g) and \( b_1 \) (L/g) are Langmuir parameters representing the maximum adsorption capacity and the adsorbate/adsorbent interaction constant, respectively.

The Freundlich isotherm is described by Eq. 3. The empirical model considers multilayer adsorption and can be applied on highly heterogeneous surfaces. In many cases it provides better representation of adsorption equilibrium of a single solute compared to a Langmuir isotherm (Merk et al., 1981), where the heat of adsorption depends on the concentration in the solid phase.

\[ q_e = k_f C_e^{1/n_F} \]  
(3)

\( q_e \) is the amount of solute adsorbed per unit mass of adsorbent (mg/g), \( k_f \) is the equilibrium constant of the Freundlich model related to adsorption capacity (L/g), \( C_e \) is the adsorbate concentration at equilibrium (mg/L), and \( n_F \) is a dimensionless exponent of the Freundlich equation related to the intensity of adsorption.

2.6. Kinetic adsorption

Adsorption kinetics describe the rate of solute removal in the fluid phase over time and are dependent on the physical and chemical characteristics of the adsorbate, the adsorbent, and the experimental system. The adsorption mechanism in adsorbents may involve the following steps: the transfer of adsorbate molecules from the solution to the external surface of the adsorbent (boundary layer); the adsorption of the adsorbate molecules into the external surface of the particle through molecular interactions; the diffusion of adsorbate molecules from the external surface to the interior of the particle (effective diffusion); and the adsorption inside the particle (Ruthven, 1984). According to Sun & Xiangjing (1997), the first stage of adsorption can be affected by increased adsorbate concentration and shaking, accelerating diffusion of the adsorbate to the solid surface. The second stage is dependent on the nature of adsorbate molecules. The third stage is generally considered the determining step, especially in the case of microporous adsorbents.

Kinetic adsorption models can be used to determine the mechanisms and adsorbent efficiency in the removal of contaminants. In this study, data relating to the adsorption of 2,4-D by soil has been treated using three kinetic models - the pseudo first-order, pseudo second-order, and intraparticle diffusion models.

Pseudo first-order Lagergren model (Khaled et al., 2009; Xu et al., 2013; Ho & McKay, 1998; Roy et al., 2013; Gualnazi et al., 2005) is the first known equation to describe the adsorption rate based on adsorption capacity. According to some authors, the pseudo first-order model may be related to the occurrence of physical adsorption, which can control the reaction rate (Ho & McKay, 1999).

---

**Table 1 - Experimental conditions used and kinetic study.**

| Experiment       | Concentration 2,4-D (mg/L) | Time (min) |
|------------------|-----------------------------|------------|
| Kinetic study    |                             |            |
| 1                | 1087.20                     | 480        |
| 2                | 6352.80                     |            |
| 3                | 4734.40                     |            |
| 4                | 8318.40                     |            |
| 5                | 10176.00                    |            |
| 6                | 17920.00                    |            |
| Equilibrium study|                             |            |
| 1                | 0.0                         | 45         |
| 2                | 1668.80                     |            |
| 3                | 4734.40                     |            |
| 4                | 8318.40                     |            |
| 5                | 10176.00                    |            |
| 6                | 17920.00                    |            |
The linear equation of Lagergren or pseudo first-order equation is expressed in Eq. 4:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2303} t$$  \hspace{1cm} (4)$$

where \(q_e\) is the adsorption capacity at equilibrium (mg/g), \(q_t\) is the adsorption capacity in time \(t\) (mg/g), \(k_1\) is the constant of the adsorption rate of pseudo first order (1/min), and \(t\) is the time of reaction (min).

Another kinetic model evaluated was the pseudo second-order model (Roy et al., 2013; Gulnaz et al., 2005; Khaled et al., 2009; Ho & McKay, 1999; Xu et al., 2013), being a linear model represented by Eq. 5:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (5)$$

where \(t\) is the time of reaction (min), \(q_t\) is the adsorption capacity in time \(t\) (mg/g), \(k_2\) is the constant of the adsorption rate of pseudo second order (g/mg.min), and \(q_e\) is the adsorption capacity at equilibrium (mg/g).

The intraparticle diffusion model is commonly expressed by Eq. 6 (Roy et al., 2013; Ho e McKay, 1998):

$$q_t = k_D t^2$$  \hspace{1cm} (6)$$

where \(q_t\) is the adsorption capacity in time \(t\) (mg/g), \(k_D\) is the velocity constant of intraparticle diffusion (mg/g.min) and \(t\) is the time of reaction (min).

Based on the assumption that 2,4-D is transported from the aqueous solution to the adsorbent by intraparticle diffusion, this is another kinetic model that must be used to study the adsorption of this contaminant in soil. The intraparticle diffusion velocity constant \((k_D)\), also known as the Weber and Morris constant, is obtained by the linearization of Eq. 6 corresponding to the angular coefficient of the line, which can present two or more linear steps that can limit the adsorption, as follows:

a) Linear stage that begins with a rapid diffusion on the outer surface of the particle;

b) Linear stage that begins with gradual adsorption, where intraparticle diffusion is the limiting rate; and

c) The equilibrium stage in which the intraparticle diffusion begins to decay due to the low solute concentration in the solution and the lower availability of adsorption sites (Chen et al., 2003).

All the experimental results for the adsorption equilibrium of the 2,4-D compounds were adjusted using the least squares method with version 7.0 STATISTICA software, applying the Langmuir and Freundlich models. The statistical significance adopted for fitting the experimental data to the models was 95 %.

3. Results and Discussion

3.1. Soil characterization

Table 2 shows pH, moisture content, density, micronutrients and organic matter content of the soil sample.

High moisture content of the superficial soil layer (0-10 cm) is due to pluviometric precipitations that occurred in the days prior to the collection of the material. According to Streck et al. (2008), the latosols have low nutrient content and high acidity, with pH below 4.9 in the superficial layer and, at greater depths, values close to 5.5 (Brazil, 1973).

Fig. 1 shows the particle size distribution of the soil sample, with clay, silt and fine sand contents, corresponding to 38,26 %, 12,83 % and 47,33 %, respectively.

3.2. Equilibrium studies

Langmuir and Freundlich adsorption isotherms were obtained using the adsorption tests with different initial concentrations of 2,4-D. Fig. 2 shows the results of experimental adsorption isotherms for 2,4-D, adjusted using the Langmuir and Freundlich models.

Adsorption isotherms for 2,4-D in soil were described as type L, according to Giles et al. (1960) classification. Fig. 2 indicates that for lower concentrations of agrochemicals added to the soil, adsorption occurs with greater intensity, indicating the affinity of the adsorbent with 2,4-D. This is confirmed by Pavlovic et al. (2005), who showed that in this isothermal shape (L) monofunctional adsorbate is strongly attracted to an adsorbent, mainly via electrostatic or ion-ion interactions, thus reaching the saturation value. By means of the experimental results, it was still possible to observe that when the lowest concentration of 2,4-D (1668.80 mg/L) was used, a removal of approximately 25.00 % was obtained, and as the concentration of the contaminant was increased (17920.00 mg/L), there was a decrease in removal to 4.50 %.

The parameters obtained by the Langmuir and Freundlich models are shown in Table 3. Considering the parameters of the models presented in Table 3, calculated with the experimental data obtained by the chromatographic analysis of 2,4-D, it is possible to verify that the Freundlich model showed better adjustment for the adsorption process.

### Table 2 - Soil characteristics: pH, moisture content, micronutrients and organic matter.

| Parameter       | Moisture content (%) | Density (g/cm³) | Micronutrients (mg/dm³) | Organic matter content (%) |
|-----------------|----------------------|-----------------|-------------------------|---------------------------|
| pH              | 4.21 ± 0.11          | 50.85 ± 4.88    | 7.580.50                | 3.17 ± 0.71               |
| Density         | 1.22 ± 0.50          | 1.52 ± 0.20     | 1.47 ± 0.01             | 0.36 ± 0.03               |
| Micronutrients  | Fe                   | Cu              | Mn                      | Zn                        |
| Fe              | 1.52 ± 0.20          | 1.47 ± 0.01     | 0.36 ± 0.03             | 3.17 ± 0.71               |
| Cu              | 1.47 ± 0.01          |                 |                         |                           |
| Mn              | 0.36 ± 0.03          |                 |                         |                           |
| Zn              | 3.17 ± 0.71          |                 |                         |                           |
of 2,4-D in the soil, based on the value of the determination coefficient ($R^2$). Considering the model, it can be assumed that the soil studied has heterogeneous sites and that the adsorption process occurs in multiple layers.

In adsorption studies of 2,4-D (25 °C) in adsorbents such as illite, sand, and humic acid, Haque & Sexton (1968) obtained values of 1.02, 1.454, and 1.09 L/mg, respectively, for the equilibrium constant of the Freundlich model ($k_F$). Delle Site (2000) reports that for values of $n_F > 1$ it is possible to have L-shaped isotherms and that the lower this ratio, the greater the interaction between adsorbate and adsorbent. This shows that due to the high $n_F$ determined in the present study, the ratio becomes smaller when compared to studies cited above, and therefore there is a high interaction between adsorbate and adsorbent.

More information can be gathered using the equilibrium constant of the Freundlich model. Alfonso et al. (2017) evaluated the adsorption of four organophosphorus pesticides (diazinon, dimethoate, methyl parathion, and sulfofetop) in different soils from Yucatán, Mexico. Their results indicate that all agrochemicals had low adsorption in the soil studied and therefore high mobility. The Freundlich model provided the best correlations, with $k_F$ in the range of 1.62-2.35 L/mg for sulfofetop, 2.43-3.25 L/mg for dimethoate, 5.54-9.27 L/mg for parathion, and 3.22-5.17 L/mg for diazinon.

These values, found by Alfonso et al. (2017), are much lower than the values observed in this research, indicating a good adsorption capacity and a higher affinity of 2,4-D for the aluminoferric red oxisol. The increased values for the two constants of the Freundlich model ($n_F$ and $k_F$) are related due to the presence of a higher clay and silt content in the studied soil, being 38.26 % and 12.83 %, respectively. According to Bekbölet et al. (1999), who investigated the adsorption of 2,4-D in soils with low organic matter and neutral pH, it has been also verified that the adsorption process is positively correlated with the organic matter content and the amount of clay and silt. This is also confirmed by Alfonso et al. (2017), who obtained the lowest and highest values of $n_F$ and $k_F$, respectively, for soil with higher clay content.

### 3.3. Adsorption kinetics

Fig. 3 shows the behavior of 2,4-D adsorption kinetics using two different initial concentrations (6352.80 mg/L and 1087.20 mg/L), in order to evaluate the equilibrium time between the adsorbent and the adsorbate used. This equilibrium time was also used to construct the adsorption isotherms. Fig. 3 shows that the equilibrium time decreases as the concentration of the contaminant increases. Based on this result and other preliminary results, the equilibrium time chosen for the other tests concerning the adsorption isotherms was 45 min.

Through the results obtained and analyzing the studied soil, it is verified that this soil does not present micro-
porosity characteristics, being that the adsorption occurs more effectively on the surface, reaching equilibrium more quickly compared to microporous adsorbents, such as activated carbon, for example. The clay soil used in this study favors the adsorption process of the contaminant, as it presents a larger surface area when compared to sandy soils. Thus, by knowing the adsorption kinetics it is possible to determine the process control steps and the adsorption behavior of 2,4-D in the studied soil. Table 4 presents the kinetic parameters of pseudo first-order and pseudo second-order Lagergren models. These parameters were determined by establishing a linear relationship from the experimental results.

Considering the kinetic pseudo first-order and pseudo second-order models, if the \( q_e \) of the linearization is not equal to \( q_e \) obtained experimentally, then the reaction will probably not be of the analyzed order, even though this plot has high correlation with the experimental data (Khaled et al., 2009; Crini et al., 2007). Analyzing the data presented in Table 4 for the pseudo-first order model, it is verified that the \( q_e \) values obtained by the linearization are very low compared with the experimental values of \( q_e \). In addition, the \( R^2 \) determination coefficient is relatively low for most data, which indicates that 2,4-D adsorption in soil is not a first-order reaction.

Fig. 4 shows the adjustments of the pseudo second-order adsorption kinetics obtained for this study.

The higher determination coefficient (\( R^2 \)) (shown in Table 4) for the pseudo-second order model shows that it provided a better adjustment to the experimental data than the pseudo first-order model. In addition, the \( q_e \) (mg/g) calculated using this kinetic model is close to the experimental \( q_e \) (mg/g).

Salman & Hameed (2010) studied adsorption kinetics for the removal of 2,4-D from contaminated water using coal and found that the pseudo second-order model fits the experimental data best. This same behavior has been observed in the work of Trivedi et al. (2016) in which peanut shells were used in the removal of 2,4-D.

In addition, the pseudo second-order model may be related to the occurrence of chemical adsorption, which can control the reaction rate (Ho & McKay, 1998). According to Ruthven (1984), in the case of chemisorption, it involves the exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent, resulting in a chemical reaction. This results essentially in a new chemical bond and therefore much stronger than in the case of the physisorption. The concepts of chemisorption and physisorption are distinct, however the two adsorption mechanisms are not completely independent. The distinction as to whether the species is physically or chemically adsorbed is not very clear, since both processes can often be described in terms of the principles of physical adsorption.

In general, the differences between physical adsorption and chemical adsorption can be summarized as: Chemical adsorption is highly specific and not all solid surfaces have active sites capable of chemically adsorbing adsorbate. It should be noted that not all molecules present in the fluid can be adsorbed chemically, only those capable of binding to the active site. Physical adsorption, unlike chemical adsorption, is non-specific. From a thermodynamics point of view, the heat involved in the physisorption is generally below 10 kcal/mol, that is, of the order of condensation/vaporization. In the adsorption chemistry, the heat of adsorption is of the order of the heat of reaction, therefore above 20 kcal/mol. It should be added that, since no formation or breakage occurs, the chemical nature of adsorbate is not altered (Nascimento et al., 2014).

In general, it was verified that the kinetic pseudo second-order model is adequate to describe the adsorption process of 2,4-D in the soil in the present study.

### Table 4 - Adsorption rate constants of pseudo first-order and pseudo second-order models and \( q_e \) values for different initial 2,4-D concentrations: adsorbate weight, 2.5 g; volume, 50 mL; temperature, 23 °C ± 1 °C.

| 2,4-D concentration (mg/L) | \( q_e \) experimental (mg/g) | \( k_1 \) (1/h) | \( q_e \) (mg/g) | \( R^2 \) | \( k_2 \) (g/mg.h) | \( q_e \) (mg/g) | \( R^2 \) |
|--------------------------|-------------------------------|----------------|----------------|-------------|-----------------|----------------|-------------|
| 6352.80                  | 14.59                         | 0.70           | 6.24           | 0.22        | 9.25            | 10.96          | 0.85        |
| 1087.20                  | 20.69                         | 0.08           | 6.01           | 0.07        | 1.00            | 16.83          | 0.99        |

### Figure 4 - Results of pseudo second-order kinetic: adsorbate weight, 2.5 g; volume, 50 mL; temperature, 23 °C ± 1 °C.
section on kinetic adsorption (methodology) and separated by the 3 vertical lines highlighted (Fig. 5). In all cases, the quality of the adjustments obtained is defined by the determination coefficient ($R^2$) for each of the steps.

Table 5 shows the adsorption kinetic constants of the model for the second stage, chosen as the process control stage (highest determination coefficient mean). For the adsorption process using 2,4-D, the intraparticle diffusion model presented a $k_p$ of 12.36 and 4.42 mg/g.h for the concentrations of 6352.80 mg/L and 1087.20 mg/L respectively.

The results show that the higher the concentration used, the higher is the $k_p$ as can be seen in Fig. 5. This result is expected because the higher the concentration used, the greater the motive power for mass transfer and the higher the rate of diffusion of the contaminant in the pores of the adsorbent. This order of velocity can be attributed to the mass and molecular configuration of 2,4-D (Foust et al., 1982).

4. Conclusion

It was possible to verify that the adsorption process of 2,4-D in the aluminoferric red oxisol occurs through different attraction forces, suggesting a diversity of active sites in the soil. Among the models that describe the kinetic adsorption of the pesticide in soil, the Freundlich model provided the best adjustment ($R^2$ of 0.96). The equilibrium constant and dimensionless exponent, both of the Freundlich model, $k_f$ and $n_f$ respectively, estimated at 34.21 and 3.7, indicate affinity between the adsorbent and the adsorbate, mainly due to the clay and silt content present in the soil and the characteristics of the analyte molecule. This implies a significant reduction in the availability and mobility of the pesticide in soil. In terms of the adsorption kinetics, it has been verified that the pseudo second-order model better represented the contaminant studied. This behavior is related to the molecule of the contaminant, as other research has also related this kinetic model to the adsorption of 2,4-D, even using another substance as an adsorbent. Based on the kinetic tests, it was possible to identify the controlling stage of the process and the high values of the determination coefficient relative to the intraparticle diffusion model. This indicated that the process is strongly controlled by the second step for the concentrations evaluated, as intraparticle diffusion rate is limiting of this process.

Furthermore, the results and conclusions obtained in this study can be used as knowledge and decision making for remediation in contaminated areas, considering that the soil in natural conditions, as in this study, already has a good ability to attenuate contaminants.

References

ABNT (1984). Solo - Análise Granulométrica - NBR 7181. ABNT - Associação Brasileira de Normas Técnicas, Rio de Janeiro, Brasil, 12p. (in Portuguese).

ABNT (2016). Amostras de Solo - Preparação para Ensaios de Compactação e Ensaios de Caracterização - NBR 6457. ABNT - Associação Brasileira de Normas Técnicas, Rio de Janeiro, Brasil, 8 p. (in Portuguese).

Alfonso, L.F.; Germán, G.V.; Carmen, P.C.M. & Hossein, G. (2017). Adsorption of organophosphorus pesticides in tropical soils: The case of karst landscape of north-western Yucatan. Chemosphere, 166:292-299.

Amarante Junior, O.P.; Santos, T.C.R.; Nunes, G.S. & Ribeiro, M.L. (2003). Breve revisão de métodos de determinação de resíduos do herbicida ácido diclorofenoxiacético (2,4-D). Química Nova, 26(2):223-229. (in Portuguese)

Table 5 - Kinetic parameters of intraparticle diffusion model for 2,4-D; adsorbent weight: 2.5 g, volume: 50 mL, temperature: 23 °C ± 1 °C.

| 2,4-D concentration (mg/L) | $k_p$ (mg/g.h) | $R^2$ |
|---------------------------|----------------|-------|
| 6352.80                   | 12.36          | 0.87  |
| 1087.20                   | 4.42           | 0.99  |

Figure 5 - Adjustment of intraparticle diffusion kinetics to 2,4-D; adsorbent weight, 2.5 g; volume, 50 mL; temperature, 23 °C ± 1 °C.
ASTM (2016). Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments - D4646-16. ASTM International, Philadelphia, USA, 5 p.

Bekbölet, M.; Yenigün, O. & Yücel, I. (1999). Sorption studies of 2,4-D on selected soil. Water, Air, and Soil Pollution, 111(1-4):75-88.

Brasil (1973). Levantamento de Reconhecimento dos Solos do Estado do Rio Grande do Sul. Ministério da Agricultura, Recife, 431 p. (in Portuguese).

Brillas, E.; Calpe, J.C. & Cabot, P. (2003). Degradation of the herbicide 2,4-dichlorophenoxyacetic acid by ozonation catalyzed with Fe$^{2+}$ and UVA light. Applied Catalysis B - Environmental, 46(2):381-391.

Chen, J.P.; Wu, S. & Chong, K. (2003). Surface modification of a granular activated carbon by citric acid enhancement of copper adsorption. Carbon, 41(10):1979-1986.

Cotillas, S.; Sáez, C.; Cañizares, P.; Cretescu, I. & Rodrigo, M.A. (2018). Removal of 2,4-D herbicide in soils using a combined process based on washing and adsorption electrochemically assisted. Separation and Purification Technology, 194:19-25.

Embrapa (2009). Manual de análises químicas de solos, plantas e fertilizantes 2ª ed. Silva, F.C. (ed), Embrapa Informação Tecnológica, Brasília, 627 p. (in Portuguese).

Foust, S.A.; Wenzel, L.A.; Clump, C.W.; Maus, L. & Andersen, L.B. (1982). Princípios das Operações Unitárias 2ª ed. LTC, Rio de Janeiro, 682 p. (in Portuguese).

Giles, C.H.; MacEwan, T.H.; Nakhwa, S.N. & Smith, D. (1960). Studies in adsorption: Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface area of solids. Journal of the Chemical Society, 3973-3993.

Gulnaz, O.; Saygideger, S. & Kusvuran, E.J. (2005). Study of Cu (II) biosorption by dried activated sludge: Effect of physico-chemical environment and kinetics study. Journal of Hazardous Materials, 120(1-3):193-200.

Haque, R. & Sexton, R. (1968). Kinetic and equilibrium study of the adsorption of 2,4-dichlorophenoxyacetic acid on some surfaces. Journal of Colloid and Interface Science, 27(4):818-827.

Ho, Y.S. & McKay, G. (1998). Sorption of dye from aqueous solution by peat. Chemical Engineering Journal, 70(2):115-124.

Ho, Y.S. & McKay, G. (1999). Pseudo-second order model for sorption process. Process Biochemistry, 34(5):451-465.

Khaled, A.; Nemr, A.E.; El-Sikaily, A. & Abdelwahab, O. (2009). Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies. Journal of Hazardous Materials, 165(1-3):100-110.

Kodeová, R.; Kocárek, M.; Kode, V.; Drábek, O.; Kozák, J. & Hettmánková, K. (2011). Pesticide adsorption in relation to soil properties and soil type distribution in regional scale. Journal of Hazardous Materials, 186(1):540-550.

Long, F.; Zhu, A.; Shi, H.; Sheng, J. & Zhao, Z. (2015). Adsorption kinetics of pesticide in soil assessed by optofluidics-based biosensing platform. Chemosphere, 120:615-620.

Mancuso, M.A.C.; Negrisol, E. & Perim, L. (2011). Efeito residual de herbicidas no solo (“Carryover”). Revista Brasileira de Herbicidas, 10(2):151-164 (in Portuguese).

Martins, C.X.; Salvador, P.M.; Jesus, J.D.; Ferreira, L.F.R.; Américo, J.H.P. & Torres, N.H. (2014). Análise de atrazina em amostras de água e solo por cromatografia gasosa (GC-ECD). Bioenergia em Revista: Diálogos, 3(1):128-138. (in Portuguese).

McKay, G.; Blair, H.S. & Gardner, J.R. (1982). Adsorption of dyes on chitin. I. Equilibrium studies. Journal of applied Polymer Science, 27(8):3043-3057.

Merk, W.; Fritz, W. & Schlünder, E.U. (1981). Competitive adsorption of two dissolved organics onto activated carbon - III: Adsorption kinetics in fixed beds. Chemical Engineering Science, 36(4):759-764.

Nascimento, R.F.; Lima, A.C.A.; Vidal, C.B.; Melo, D.Q. & Raulino, G.S.C. (2014). Adsorção: Aspectos teóricos e aplicações ambientais. Imprensa Universitária, Fortaleza, 256 p. (in Portuguese).

Nethaji, S. & Sivasamy, A. (2017). Graphene oxide coated with porous iron oxide ribbons for 2,4- dichlorophenoxyacetic acid (2,4-D) removal. Ecotoxicology and Environmental Safety, 138:292-297.

Pavlovic, L.; Barriga, C.; Hermosín, M.C.; Cornejo, J. & Ulibarri, M.A. (2005). Adsorption of acidic pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite. Applied Clay Science, 30(2):125-133.

Piaia, B.R.; Zago, M.L.C.; Denardin, E.L.G. & Roehrs, R. (2017). Fitoremediación dos herbicidas 2,4-diclorofenoxyacético y propanil en suelo cultivado por erva cidreira (Melissa officinalis). Ciência e Natura, 39(1):91-98 (in Portuguese).

Prado, B.; Strozzi, A.G.; Huerta, E.; Duwig, C.; Zamora, O.; Delmas, P.; Casasola, D. & Márquez, J. (2016).
2,4-D mobility in clay soils: Impact of macrofauna abundance on soil porosity. Geoderma, 279:87-96.

Risco, C.; López-Vizcaíno, R.; Sáez, C.; Yustres, A.; Cañizares, P.; Navarro, V. & Rodrigo, M.A. (2016). Remediation of soils polluted with 2,4-D by electrokinetic soil flushing with facing rows of electrodes: A case study in a pilot plant. Chemical Engineering Journal, 285:128-136.

Rodríguez-Rubio, P.; Morillo, E. & Maqueda, C. (2006). Sorption of 2,4-D on natural and organic amended soils in different characteristics. Journal of Environmental Science and Health, Part B, 41(2):145-157.

Roy, A.; Adhikari, B. & Majumder, S.B. (2013). Equilibrium, kinetic, and thermodynamic studies of azo dye adsorption from aqueous solution by chemically modified lignocellulosic jute fiber. Industrial & Engineering Chemical Research, 52(19):6502-6512.

Ruthven, D.M. (1984). Principles of Adsorption and Adsorption Processes. John Wiley & Sons, New York, 433 p.

Salman, J.M. & Hameed, B.H. (2010). Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. Desalination, 256(1-3):129-135.

Shano, A.; Ferreira, J.V.R.; Peckle, B.A.; Macrae, A. & Direito, I.C.N. (2013). Otimização de método cromatográfico para quantificação do herbicida ácido 2,4-diclorofenoxiacético (2,4-D). Acta Scientiae et Technicae, 1(2):37-46. (in Portuguese)

Silva, A.A. & Silva, J.F. (2007). Tópicos em Manejo de Plantas Daninhas. Editora UFV, Viçosa, 367 p. (in Portuguese)

Souza, F.L.; Saéz, C.; Llanos, J.; Lanza, M.R.V.; Cañizares, P. & Rodrigo, M.A. (2016a). Solar-powered electrokinetic remediation for the treatment of soil polluted with the herbicide 2,4-D. Electrochimica Acta, 190:371-377.

Souza, F.L.; Saéz, C.; Lanza, M.R.V.; Cañizares, P. & Rodrigo, M.A. (2016b). Removal of pesticide 2,4-D by conductive-diamond photoelectrochemical oxidation. Applied Catalysis B: Environmental, 180:733-739.

Spadotto, C.A.; Matallo, M.B. & Gomes, M.A.F. (2003). Sorção do herbicida 2,4-D em solos brasileiros. Pesticidas: Revista de Ecotoxicologia e Meio Ambiente, 13:103-110. (in Portuguese)

Streck, E.V.; Kämpf, N.; Dalmolin, R.S.D.; Klamt, E.; Nascimento, P.C.; Schneider, P.; Giasson, E. & Pinto, L.F.S. (2008). Solos do Rio Grande do Sul, 3ª ed. Emater, Porto Alegre, 222 p. (in Portuguese)

Sun, G. & Xu X. (1997). Sunflower stalks as adsorbents for color removal from textile wastewater. Industrial & Engineering Chemistry Research, 36(3):808-812.

Trivedi, N.S.; Kharkar, R.A. & Mandavgane, S.A. (2016). 2,4-Dichlorophenoxyacetic acid adsorption on adsorbent prepared from groundnut shell: Effect of preparation conditions on equilibrium adsorption capacity. Arabian Journal of Chemistry, 7:22-31.

Vieira, E.M.; Prado, A.G.S.; Landgraf, M.D. & Rezende, M.O.O. (1999). Estudo da adsorção/dessorção do ácido 2,4 diclorofenoxiacético (2,4D) em solo na ausência e presença de matéria orgânica. Química Nova, 22(3):305-308. (in Portuguese)

Xu, M.; Yin, P.; Liu, X.; Dong, X.; Xu, Q. & Qu, R. (2013). Preparation, characterization, adsorption equilibrium, and kinetics for gold-ion adsorption of spent buckwheat hulls modified by organodiphosphonic acid. Industrial & Engineering Chemical Research, 52(24):8114-8124.

WHO (2004). Guidelines for Drinking-water Quality, Vol. 1, 3rd ed. World Health Organization, Geneva, Switzerland, p. 515.

Yue, L.; Ge, C.; Feng, D.; Yu, H.; Deng, H. & Fu, B. (2017). Adsorption-desorption behavior of atrazine on agricultural soils in China. Journal of Environmental Sciences, 57:180-189.