

Effect of pH on sorption kinetic process of acidic herbicides in a volcanic soil

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Abstract

Kinetic studies of pesticides in soil are of great importance to know the processes and parameters that govern their fate in the environment. The aim of this study was to evaluate the influence of pH on the kinetic sorption process of four acidic herbicides, clopyralid, fluroxypyr, picloram and triclopyr on an Andisol, characterized by its high organic matter content and acidic pH. The pseudo-second-order model appeared to fit the data better than other models ($R^2 > 0.999$). All herbicides were adsorbed rapidly during the first stage, but their adsorption was affected by pH and their chemical nature. The initial rates of reactions strongly decreased by increasing pH. The initial adsorption rates (h) and the sorption capacity of the herbicides showed the following order fluroxypyr > triclopyr > picloram > clopyralid. At pH 4.0 the maximum amounts of fluroxypyr, triclopyr, picloram, and clopyralid adsorbed were respectively 75.2, 69.7, 40.5 and 11.7 %. The application of Elovich and Weber-Morris models suggests that mass transfer through the boundary layer and to a lesser degree intra-particle diffusion, control sorption kinetics, which appeared to be influenced by pH and chemical nature of the herbicides. The results obtained in this work suggest that soil pH and acidic character of herbicides could strongly affect the bioavailability of these herbicides on soil and their potential leaching.

Keywords: Acidic herbicides, sorption kinetic, Andisols, kinetic models

1. Introduction

Clopyralid, fluroxypyr, picloram and triclopyr are widely used in post-emergence to control broadleaf weeds in cereals, pastures and many other crops. They are systemic herbicides absorbed by the foliage and roots of plants. They are acidic herbicides with low pK_a values (Table 1), and are then present in the anionic form within the pH range of soils and the environment (Tomlin, 1995; PPDB, 2013). Based

on their chemical properties, there is a high risk of leaching to groundwater being these herbicides moderately toxic to animals (Cessna, 2002; Antunes-Kenyon and Kennedy, 2004; Palma *et al.*, 2004; Messing *et al.*, 2011; Lazartigues *et al.*, 2013; Ulen *et al.*, 2014).

They are weakly sorbed in soil through hydrophobic interactions and hydrogen bonding onto soil organic

matter (OM), along with other suggested mechanisms for soils with low OM content (Kah and Brown, 2006). In general, it was established that the OM content and pH are the most important factors (but not independent) which affect sorption in soils. Furthermore, many authors have demonstrated that the adsorption of neutral molecule is largely influenced by the OM (Delle, 2001; Kah and Brown, 2006; Bukun *et al.*, 2010; Assis *et al.*, 2011).

Andisols are volcanic soils that are widely distributed around the world. They are variable surface charge and acidic pH soils, high in OM and allophane content. They have a high specific surface area, a low bulk density and high water retention capacity (Escudey *et al.*, 2004).

Kinetic studies of pesticides in soil are of great importance to determine the parameters and processes involved in their sorption, being of agricultural and environmental relevance.

Sorption studies are usually conducted in apparent equilibrium conditions because that although and initial rapid sorption occurs, it may take a long time before the equilibrium is reached. The interaction of an herbicide with soil is a time dependent process which defines its bioavailability in soil. Sorption kinetic is characterized by a first rapid sorption stage followed by a second slower stage. According to Fernandez-Bayo *et al* (2008) this process occurs in three stages. The first stage is the diffusion of the pesticide to the surface of the sorbent called film mass transfer or boundary diffusion. The second stage, named particle diffusion stage is slower, and is due to the diffusion of the solute within internal mesopores and micropores. The last stage, is the sorption of the solute in the interior surface of the sorbent through mass-action controlled mechanisms and rapid uptake occurs. There are few kinetic studies of pesticides in soil and particularly there are no published papers for these herbicides in Andisols, although studies

have been reported for other acidic herbicides in these variables charges soils (Espinoza *et al.*, 2009; Cáceres *et al.*, 2010b). In this work we use models to establish kinetic parameters and modeling of sorption process, such as hiperbolic pseudo-first- and pseudo-second-order and Elovich and Weber-Morris model used to describe solute transport mechanisms of organic compounds in soils (Azizian, 2004; Fernández-Bayo *et al.*, 2008; Qiu *et al.*, 2009; Cáceres *et al.*, 2010a, 2010b).

The agronomic management involves urea fertilization before herbicide application with significant pH changes in soils (Campillo and Rodriguez, 1984; Mora *et al.*, 2004; Cartes *et al.*, 2009). Changes in soil pH under these conditions could strongly modify the sorption process and consequently mobility and degradation of acidic herbicides.

The aim of this study was to evaluate the influence of pH on the kinetic sorption process of four acid herbicide, clopyralid, fluroxypyr, picloram and triclopyr on an Andisol characterized by its high organic matter content and acidic pH. Kinetic parameters were determined using the hyperbolic, pseudo-first-order and pseudo-second-order models and mechanistic aspects were analyzed using the Elovich and Weber-Morris models.

2. Materials and Methods

2.1. Herbicides

The herbicides used were: clopyralid (3,6-dichloropyridine-2-carboxylic acid), fluroxypyr (4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid), picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) and triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid). The analytical standards of herbicides were provided by Chem Service (West

Chester, USA). All reagents used were analytical or HPLC grade.

2.2. Soil

An Andisol from southern Chile, belonging to the Freire family (38° 50' S and 72° 35' W), which is medial, mesic, Typic Placudands, with a silty loam texture was used (CIREN, 2002). Soil samples were collected from the surface layer (0–20 cm), air dried, and sieved through a 2-mm mesh and characterized according to the methods described in Sadzawka *et al.*, (2006). Briefly, the OM content was measured using the Walkley - Black method. The pH was measured in soil suspensions with deionized water at 1:2.5 (w/v) ratio and with 0.01 M CaCl₂. Cation exchange capacity (CEC) was calculated from the total exchangeable bases (Mg, Ca, K, and Na extracted by 1 M ammonium acetate at pH 7.0) and analyzed by flame atomic absorption spectrophotometry. Table 2 shows the main properties of the Andisol under investigation.

2.3. Adsorption kinetics

Duplicate sample of 2.0 g soil were placed in 50 mL centrifuge tubes (polypropylene copolymer), and mixed with approximately 18 mL of a 0.01 M CaCl₂ aqueous solution. Small volumes of HCl and NaOH 1 M were added to adjust pH at 4.0, 5.0 and 6.0. Preliminary tests were conducted in presence of herbicides to determine the minimum volume of acid or alkali solution required to reach pH 4, 5 or 6. Finally, each herbicide prepared in a 0.01 M CaCl₂ aqueous solution was added to result in a concentration of 1.0 mg L⁻¹ in a final volume of 20 mL. The tubes were shaken at 20±1°C in a rotary shaker for 1-24 hours. Subsamples were removed at different intervals of times, centrifuged at 2065g for 15 min and filtered using 0.22 µm membranes (Durapore, PVDF from

Millipore) and transferred to HPLC vials for analysis. Sorption experiments were repeated twice. For all experiments the final pH was 4, 5 or 6 ± 0.1.

2.4. Herbicide analysis

The herbicides were analyzed using a Shimadzu Prominence HPLC chromatograph LC-20AT with a diode array detector (SPD-M20A), using a prontoSil column RP-C18 (250x4.6 mm). The mobile phase used was a 50:50 (v/v) mix of acetonitrile and water acidified to pH 2 with phosphoric acid. The detection wave-length was 225 nm for all herbicides. The injection volume was 20 µL, the flow 1.0 mL min⁻¹ and the oven temperature 30 °C. Calibration curves were prepared for each herbicide.

2.5. Kinetic models

2.5.1. Hyperbolic model

The linear form of this model (Equation 1) enables us to obtain some sorption parameter values by fitting it to experimental data. Where q_t is the sorbed quantity (mg kg⁻¹) at time t ; q_{max} (mg kg⁻¹) is the maximum sorbed amount; t (h) is the solid-solution contact time, and B is an empirical constant.

$$\frac{1}{q_t} = \frac{B}{q_{max}} \frac{1}{t} + \frac{1}{q_{max}} \quad (1)$$

2.5.2. Pseudo-first-order kinetic reaction model

Some sorption parameter by fitting it to the experimental data, where obtained, q_t (mg kg⁻¹), q_{max} (mg kg⁻¹), are similarly defined as in the hyperbolic model, and k_f (h⁻¹) correspond to the first-order rate constant (Equation 2)

$$\log(q_{max} - q_t) = \log q_{max} - \frac{k_1}{2.303} t \quad (2)$$

2.5.3. Pseudo-second-order kinetic reaction model

This model (Equation 3) assumes that the sorption capacity could be proportional to the number of active soil sites, where q_t and q_{max} have the same definition as in the previous models and k_2 ($\text{mg kg}^{-1} \text{h}^{-1}$) is the reaction-rate constant.

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

2.5.4. Elovich equation

This equation establishes that the sorption kinetics take place in two phases. A rapid initial stage associated with the movement of the pesticide to the most accessible parts of the soil, followed by a slower second stage where diffusion particles in soil micropores occur. The linear form is written in Equation 4, where q_t is the sorbed quantity (mg kg^{-1}) at time t , and X and Y are empirical constants. The intersect ($1/Y \ln(X/Y)$) correspond to the sorbed quantity for the fast phase and the slope $1/y$, represents the duration of second phase.

$$q_t = \frac{1}{Y} \ln(xy) + \frac{1}{Y} \ln t \quad (4)$$

2.5.5. Weber-Morris model

This equation (Equation 5) establishes that many sorption processes vary proportionally with $t^{1/2}$, where q_t is the pesticide adsorbed (mg kg^{-1}) at time t , C (mg kg^{-1}) is a constant related to the thickness of the boundary layer and k_{int} ($\text{mg kg}^{-1} \text{h}^{-1/2}$) is the intra-particle diffusion rate constant.

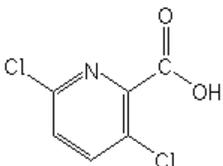
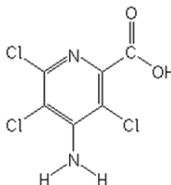
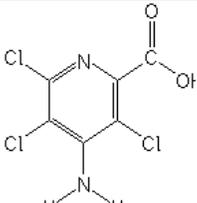
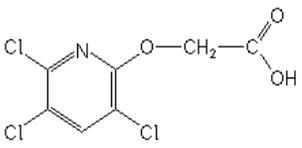
$$q_t = k_{int} t^{1/2} + C \quad (5)$$

3. Results and Discussion

The effect of pH on the equilibrium between neutral and anionic forms of both herbicides is shown in Table 1. This relationship, pKa-dependent, is fundamental to understand the sorption processes of these acidic herbicides on soils. Neutral form of each herbicide were present at pH 4.0, but their concentration decreasing by increasing pH. The percentages of neutral forms of clopyralid, fluroxypyr, picloram and triclopyr at pH4 were approximately 1, 7, 2.0 and 50% respectively (Schwarzenbach *et al.*, 2003).

For these herbicides no kinetics studies are reported in literature. However, some authors ascertained that the adsorption of these herbicides was affected by OM and pH and that these substances were weakly sorbed on OM through hydrophobic interactions and hydrogen bonding (Delle, 2001; Kah and Brown, 2006, 2007; Bukun *et al.*, 2010; Assis *et al.*, 2011).

Table 1. Some properties of herbicides

Herbicide	Formula	Sw ^a (g L ⁻¹)	Log P ^b	pK _a	α ^c (%)		
					pH 4	pH 5	pH 6
Clopyralid		143	-2.63	2.0	0.99	0.1	0.01
Fluroxypyr		0.09	0.04	2.9	7.4	0.8	0.1
Picloram		0.6	-1.92	2.3	2.0	0.2	0.02
Triclopyr		8.0	4.62	4.0	50.0	9.1	1.0

^a Water solubility. ^bLog P, octanol-water partition coefficient. ^cneutral form of herbicide (%). (Source: Tomlin 1995; PPDB,2013).

Figure 1, 2, 3, 4 show the sorption kinetics of clopyralid, fluroxypyr, picloram and triclopyr, respectively at pH 4, 5 and 6. The sorption capacity of these herbicides was in the order fluroxypyr > triclopyr > picloram > clopyralid. The quantities of clopyralid adsorbed in the first 15 minutes at pH 4, 5 and 6 was 8.6, 4.0 and 2.0%, respectively. (Figure 1). For fluroxypyr they were 67.8, 50.5 and 33.6%. (Figure 2). For picloram 34.1, 18.9 and 13.0% (Figure 3)

and, finally, for triclopyr 60.2, 38.3 and 26.6%. (Figure 4). The sorption of all the herbicides increased quickly during this short herbicide solution-soil contact time, followed by much slower stage progressing towards an apparent equilibrium to 24 hours. After 24 hours, at pH 4, the amount of clopyralid, fluroxypyr, picloram and triclopyr, adsorbed were 11.7, 75.2, 40.5 and 69.7%, respectively.

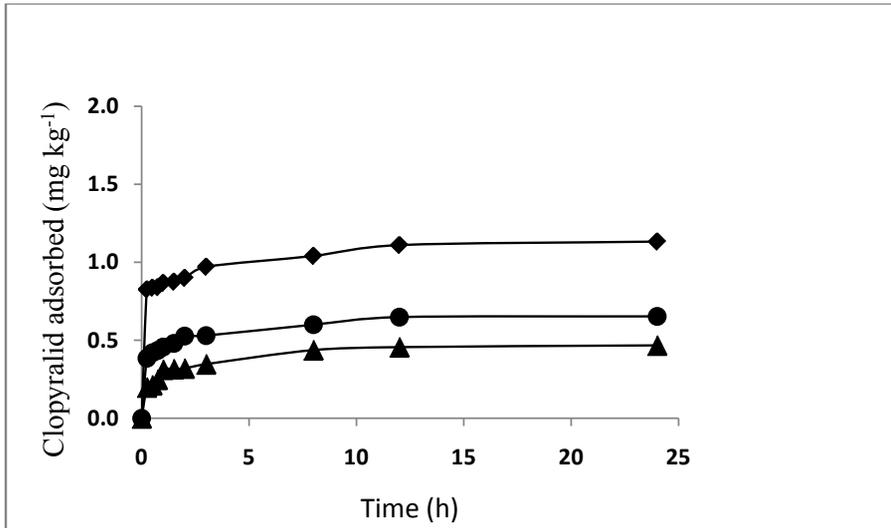


Figure 1. Sorption kinetics of clopyralid at pH 4 (◆), pH 5 (●) and pH 6 (▲)

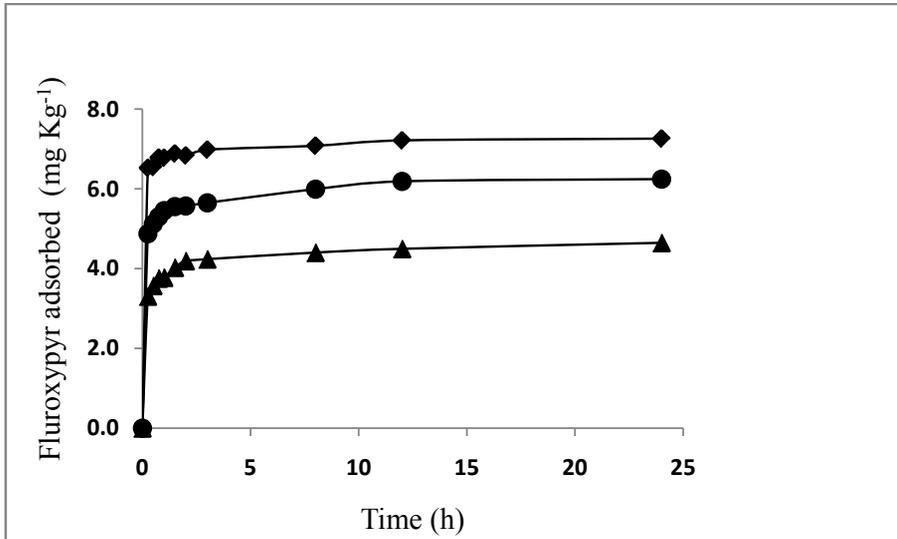


Figure 2. Sorption kinetics of fluroxypyr at pH 4 (◆), pH 5 (●) and pH 6 (▲)

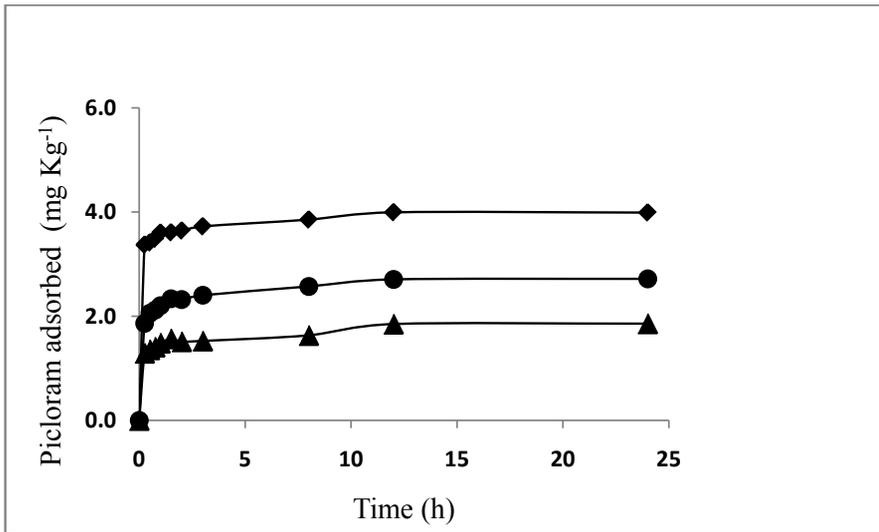


Figure 3. Sorption kinetics of picloram at pH 4 (♦), pH 5 (●) and pH 6 (▲)

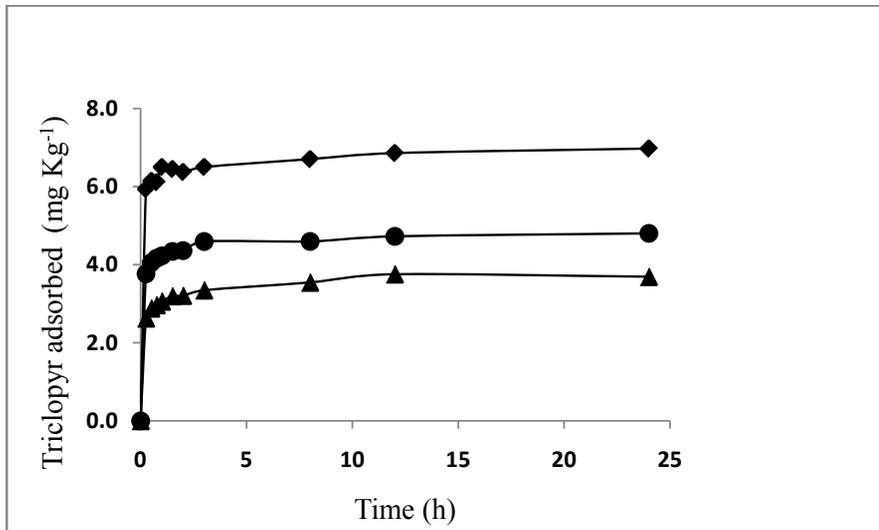


Figure 4. Sorption kinetics of triclopyr at pH 4 (♦), pH 5 (●) and pH 6 (▲)

These results are in accordance with some properties of herbicides reported in Table 1, as log P, which indicates a greater hydrophobic character for triclopyr and fluroxypyr compared to picloram and clopyralid. Besides, within the range of pH studied, the percentages of neutral form of triclopyr and fluroxypyr are much higher than those of picloram and clopyralid. Furthermore at low pH values picloram and fluroxypyr may be partially in cationic form due to protonation of amino groups with a consequent higher adsorption capacity of these herbicides (Assis *et al.*, 2011). On the other hand, it is known that the pH in the soil surface may be lower than in the soil solution, meaning that a higher number of neutral herbicide molecules could be available to be adsorbed. On the surface of OM the pH might be 0.2-0.5 unit lower than liquid phase. Kinetic studies carried out on Andisol for metsulfuron-methyl (Caceres 2010a), atrazine (Baez *et al.*, 2013) and diuron (Caceres *et al.*, 2013) have shown similar behavior, with a rapid initial stage followed by a slower second stage to reach an apparent equilibrium over time.

Different kinetic models were applied to the experimental data in order to determine the kinetic parameters and information on the adsorption mechanisms involved (Table 3, 4).

For hyperbolic model the determination coefficients (R^2), used to evaluate the model fit were lower ($0.70 < R^2 < 0.89$), although q_{\max} values are near experimental values (Table 3, 4). For pseudo-first-order model the R^2 values showed a good fit ($0.86 < R^2 < 0.99$). However, the q_{\max} value given by the model differed largely from experimental $q_{\max\text{exp}}$ estimated from experimental data at 24 hours (Table 3, 4).

The pseudo-second-order model shows a good fit with the experimental data, with R^2 values > 0.99 for all pHs and herbicides. The q_{\max} values obtained are consistent with experimental values (Table 3,

4). For the four herbicides, clopyralid showed the highest kinetic rate constant (k_2). There are marked differences in the first stage of the adsorption process according to the values of the initial rate constant ($h = q_{\max}^2 k_2$), obtained from the intercept of pseudo-second-order equation (Equation 3). In general, h showed the following order fluroxypyr $>$ triclopyr $>$ picloram $>$ clopyralid. At pH 4, where there are a greater amount of neutral molecules of herbicides, h values approximately were 83, 50, 28 and 3.0 $\text{mg kg}^{-1} \text{h}^{-1}$ (Table 3, 4). At higher pHs, the initial rate deeply decreased for all herbicides.

The Elovich model (Equation 4), used to describe the pseudo-second-order kinetics fit well for all herbicides ($R^2 > 0.92$) (Table 3, 4). From the Elovich linear equation, the intercept ($1/Y$) ($\ln XY$) is considered the amount sorbed during initial equilibrium phase (fast phase reaction) and $1/Y$ is the sorption rate as a function of time during the slow phase of the reaction (Caceres *et al* 2010a). The herbicide amount sorbed during the fast phase ranged between 92-82, 90-81, 89-78 and 77-58% of the total sorbed amount, for fluroxypyr, triclopyr, picloram and clopyralid, respectively, indicating an almost instantaneous adsorption equilibrium for all herbicides, except clopyralid, which present the lowest h value.

In general, coefficient ($1/Y$) values for all herbicides were very lower compared with h values and no dependence with pH was obtained (Table 3, 4).

The Weber-Morris model relates q_t versus $t^{1/2}$ generating straight line that passes through the origin (Equation 5) when the intra particle diffusion process controls the sorption mechanism. C intercept values provide information relate of the thickness of the boundary layer, a larger value meaning a higher boundary layer effect. Table 3 and Table 4 shows the kinetic parameters obtained for this model. The model shows a good fit for all herbicides ($0.76 < R^2 < 0.94$), but the line no pass through the origin, with C values different to zero. Then,

the boundary layer that surround soil particles have an important effect on the initial sorption kinetics for all herbicides, being the lowest for clopyralid. These results are in accordance with those obtained for Cáceres *et al.* (2010a) who studied the sorption behavior of metsulfuron-methyl (pKa = 3.3) on Andisols. In these soils, mass transfer across the boundary layer, and in a lesser degree, intraparticle diffusion were the two processes that control sorption kinetic. In this study,

Cáceres *et al.* (2010a) compared the herbicide behavior in Ultisols and Andisol concluding that the mineral fraction and OM, respectively define the processes that control sorption kinetic. In Ultisols intraparticle diffusion was the mainly processes. Others studies on the adsorption of atrazine (weak base) and diuron (Baez *et al.*, 2013; Cáceres *et al.*, 2013) on Chilean Andisols and Ultisols have shown a behavior similar to that of metsulfuron-methyl in these soils.

Table 2. Selected properties of studied Andisol soil

pH _{H2O}	pH _{CaCl2}	OM ^a (%)	CEC ^b (cmol ₍₊₎ /kg)	Sand (%)	Silt (%)	Clay (%)	Texture
5.68	4.76	15.0	8.20	39.7	42.9	17.3	Silty loam

Mean Values, *n* = 3. ^aOrganic matter. ^bCation exchange capacity.

Table 3. Kinetic parameters from linear analysis of hiperbolic model, pseudo-first-order, pseudo-second-order, Weber-Morris and Elovich kinetic models of fluroxypyr and triclopyr on Andisol soil at pH 4, 5 and 6

Herbicide	Fluroxypyr			Triclopyr		
	4	5	6	4	5	6
q _{max exp} (mg kg ⁻¹)	7.26± 0.04 ^a	6.24± 0.02	4.65± 0.12	6.97± 0.060	4.80± 0.01	3.69± 0.04
Hiperbolic						
q _{max} (mg kg ⁻¹)	7.09 ± 0.12 ^b	5.92 ± 0.20	4.39 ± 0.16	6.71 ± 0.20	4.63 ± 0.20	3.50 ± 0.18
R ²	0.732	0.818	0.881	0.740	0.895	0.854
Pseudo-first-order						
q _{max} (mg kg ⁻¹)	0.69 ± 0.16	1.07 ± 0.06	1.07 ± 0.03	1.04 ± 0.03	0.72 ± 0.08	0.79 ± 0.03
k ₁ (h ⁻¹)	0.14 ± 0.04	0.18 ± 0.01	0.17 ± 0.01	0.24 ± 0.01	0.20 ± 0.01	0.10 ± 0.02
R ²	0.981	0.988	0.960	0.944	0.963	0.903
Pseudo-second-order						
q _{max} (mg kg ⁻¹)	7.30 ± 0.01	6.29 ± 0.01	4.67 ± 0.02	6.99 ± 0.01	4.83 ± 0.01	3.75 ± 0.02
k ₂ (kg mg ⁻¹ h ⁻¹)	1.56 ± 0.02	0.84 ± 0.02	0.90 ± 0.02	1.02 ± 0.01	1.30 ± 0.02	1.21 ± 0.02
h (mg kg ⁻¹ h ⁻¹)	83.33	33.33	19.61	50.00	30.30	16.95
R ²	0.999	0.999	0.999	0.999	0.999	0.999
Elovich						
(1/y)lnxy (mg kg ⁻¹)	6.76 ± 0.04	5.37 ± 0.01	3.82± 0.02	6.29 ± 0.2	4.20 ± 0.03	3.04 ± 0.02
1/y (mg kg ⁻¹)	0.17 ± 0.02	0.30 ± 0.02	0.29 ± 0.02	0.22 ± 0.01	0.21 ± 0.01	0.24 ± 0.00
R ²	0.956	0.981	0.955	0.926	0.939	0.968
Weber-Morris						
k _{int} (mg kg ⁻¹ h ^{1/2})	0.16 ± 0.02	0.29 ± 0.02	0.27 ± 0.02	0.21 ± 0.01	0.20 ± 0.03	0.23 ± 0.02
C (mg kg ⁻¹)	6.59 ± 0.10	5.06 ± 0.10	3.54 ± 0.08	6.06 ± 0.20	3.99 ± 0.40	2.80 ± 0.10
R ²	0.837	0.853	0.779	0.827	0.756	0.812

q_{max exp} at 24 h. ^bStandard deviations for *n*=4

Table 4. Kinetic parameters from linear analysis of hiperbolic model, pseudo-first-order, pseudo-second-order, Weber-Morris and Elovich kinetic models of clopyralid and picloram on Andisol soil at pH 4, 5 and 6

Herbicide	Clopyralid			Picloram		
	pH 4	pH 5	pH 6	pH 4	pH 5	pH 6
$q_{\max \text{ exp}} \text{ (mg kg}^{-1}\text{)}$	$1.14 \pm 0.04^{\text{a}}$	0.66 ± 0.04	0.47 ± 0.02	4.00 ± 0.02	2.72 ± 0.02	1.86 ± 0.01
$q_{\max} \text{ (mg kg}^{-1}\text{)}$	$0.99 \pm 0.20^{\text{b}}$	0.57 ± 0.20	0.40 ± 0.20	3.82 ± 0.12	2.55 ± 0.20	1.67 ± 0.16
R^2	0.732	0.769	0.837	0.704	0.865	0.714
Pseudo-first-order						
$q_{\max} \text{ (mg kg}^{-1}\text{)}$	0.34 ± 0.12	0.25 ± 0.08	0.23 ± 0.04	0.57 ± 0.02	0.67 ± 0.02	0.54 ± 0.03
$k_1 \text{ (h}^{-1}\text{)}$	0.20 ± 0.01	0.09 ± 0.01	0.10 ± 0.01	0.15 ± 0.01	0.22 ± 0.01	0.15 ± 0.00
R^2	0.994	0.874	0.857	0.959	0.968	0.933
Pseudo-second-order						
$q_{\max} \text{ (mg kg}^{-1}\text{)}$	1.14 ± 0.01	0.66 ± 0.01	0.48 ± 0.02	4.02 ± 0.01	2.75 ± 0.01	1.87 ± 0.02
$k_2 \text{ (kg mg}^{-1} \text{h}^{-1}\text{)}$	2.30 ± 0.02	3.18 ± 0.02	2.84 ± 0.02	1.72 ± 0.01	1.35 ± 0.02	1.41 ± 0.02
$h \text{ (mg kg}^{-1} \text{h}^{-1}\text{)}$	3.00	1.40	0.66	27.78	10.20	4.95
R^2	0.999	0.999	0.999	0.999	0.999	0.998
Elovich						
$(1/y) \ln xy \text{ (mg kg}^{-1}\text{)}$	0.88 ± 0.02	0.46 ± 0.01	0.28 ± 0.02	3.56 ± 0.02	2.19 ± 0.03	1.46 ± 0.02
$1/y \text{ (mg kg}^{-1}\text{)}$	0.08 ± 0.02	0.06 ± 0.02	0.06 ± 0.00	0.15 ± 0.01	0.19 ± 0.00	0.12 ± 0.00
R^2	0.938	0.980	0.965	0.973	0.975	0.923
Weber-Morris						
$k_{\text{int}} \text{ (mg kg}^{-1} \text{h}^{1/2}\text{)}$	0.08 ± 0.02	0.06 ± 0.02	0.06 ± 0.02	0.15 ± 0.01	0.18 ± 0.00	0.12 ± 0.01
$C \text{ (mg kg}^{-1}\text{)}$	0.79 ± 0.06	0.38 ± 0.10	0.21 ± 0.08	3.40 ± 0.06	1.20 ± 0.04	1.32 ± 0.08
R^2	0.939	0.885	0.854	0.874	0.828	0.879

^a $q_{\max \text{ exp}}$ at 24 h. ^b Standard deviations for $n=4$

4. Conclusions

Kinetic studies concluded that a large amount of all herbicides are adsorbed in the rapid first stage, depending on the pH, followed by much lower adsorption in the slower second stage. The kinetic data was found to follow closely the pseudo-second-order kinetic model. In Andisols, characterized by a high content of organic matter is the its main characteristic, the mass transfer across the boundary layer, and, in a lesser degree, intraparticle diffusion mechanisms controlled the adsorption kinetics of the herbicides. The adsorption kinetic was affected by pH and chemical nature of the herbicides, according the pseudo-second-order kinetic reaction, Elovich and Weber-Morris models. These results suggest that soil pH and chemical nature of the herbicide could have a strong influence on their mobility in soils and then on their bioavailability.

Acknowledgments

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