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Hydrodispersive parameters determination of potassium in soil fertilised with vinasse

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Abstract

Vinasse is one of the byproducts of alcohol distillation, being a combination of nutrient contents, which can act on the soil and plant when used as fertiliser. This work aimed to determine the hydrodispersive parameters of potassium ion (K^+), applied via vinasse, in a dystrophic Yellow Ultisol cultivated with sugarcane by identifying the possible adsorption, retention, and leaching processes of this element. The miscible displacement assays were performed on saturated soil columns. The CXTFIT code was used to estimate the transport parameters of the convection-dispersion (CD) and CD two-site sorption (CD-2S) models through the experimental data. The CD-2S model represented the experimental data of the K^+ breakthrough curves for

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both columns, indicating the existence of chemical nonequilibrium, that is, sorption kinetics. The CD-2S model allowed to properly determine the retention and leaching capacity of the K^+ *ion in the soil, which showed that the vinasse dosage for a 0-20 cm layer must be controlled, to avoid its leaching and consequent groundwater contamination.*

Keywords: Potassium, vinasse, hydrodispersive parameters, CXTFIT, sugarcane

1. INTRODUCTION

The production of ethanol from sugarcane generates some byproducts that are reincorporated in the process, such as vinasse resulting from the fermentation of sugarcane juice (Carrilho, Labuto, and Kamogawa 2016; CETESB 2015). Due to its physicochemical characterisation, vinasse generally contains, in addition to organic matter, high levels of potassium, nitrate, calcium, phosphorus, and other nutrients (Possignolo et al. 2015). Thus, the vinasse began to be used to fertigate the sugarcane plantations to reduce industrial chemical fertilisers in the crops, contributing to the mitigation of impacts on the environment (FAO 2017).

On average, for each litre of alcohol produced, there are thirteen litres of vinasse used in fertigation, thanks to the presence of essential nutrients beneficial to the plant (CETESB 2015). Properly applied vinasse promotes improved soil fertility, as about 150 m^3 ha^{-1} equals fertilisation of 61 kg ha^{-1} nitrogen, 40 kg ha^{-1} phosphorus, 343 kg ha^{-1} potassium, 108 kg ha^{-1} of calcium, and 80 kg ha^{-1} of sulphur (CARVALHO et al. 2014). However, when used for this purpose, the quantities should not exceed the soil water retention capacity (Souza et al. 2015), since once the leaching of several of these elements, mainly nitrate and potassium, present in large quantities in vinasse occurs, soil pH and salinisation can be altered (Barros et al. 2010), and even cause salinisation and groundwater contamination (M. A. S. da Silva, Griebeler, and Borges 2007; W. P. da Silva et al. 2014).

Since it has a high productivity response, potassium is applied in high doses both in sugarcane and in rigs, in more significant quantities than nitrogen. Doses between 80 and 150 kg of K_2O per hectare are used for both cane-plant and brassiere.

However, the application of potassium without knowledge of the proper dose and the mineral supplementation is insufficient to meet the nutritional needs of the crop and may even result in an imbalance of nutrients, affecting the productivity of the cane. The appropriate recommendation should be based on the soils' chemical analysis, potassium concentration in the vinasse, and the calibration curves obtained through the experimental results.

In addition to providing water and nutrients, fertigation with vinasse introduces nutrients into the subsurface soil, such as exchangeable Ca^{2+}, Mg^{2+}, and K^{+}, enriching the soil. The problem arises from the disproportion of K from the other nutrients present in vinasse. Some sugar mills noticed that by applying higher doses, profits could be expected, reducing industrial fertilisers and increasing agricultural yields. Potassium favours sugarcane vegetation and tillering, as it acts in several physiological aspects, but the excess of this nutrient can disrupt various structural and metabolic functions of the plant freitas(Freitas et al. 2017).

It is advisable to analyse the vinasse for reuse as fertiliser, based on detailed studies involving precipitation, adsorption, and pollutants' transport. Each soil has its adsorption capacity, which, if surpassed, the vinasse is potentially available for leachate and may affect surface and groundwater. This contamination depends on several factors related to the numbers of residues deposited in the soil, the concentration of these residues, the local climate (precipitation), and the soil retention capacity (Fábio L Brito, Rolim, and Pedrosa 2007; Nicochelli et al. 2012).

Vinasse can cause various changes in soil chemical properties such as pH, organic matter (OM), nutrient availability such as Potassium (K), cation exchange capacity (CEC), and electrical conductivity (F.L. Brito, Rolim, and Pedrosa 2009; A. J. N. da Silva et al. 2006; Zolin et al. 2011).

Vinasse can also improve soil aggregation, resulting in a higher water infiltration capacity into the soil (Gariglio, Matos, and Lo Monaco 2014; M. A. S. da Silva, Griebeler, and Borges 2007). According to Nicochelli et al., (2012), increasing vinasse doses increases the exchangeable K concentration, especially in the soil's superficial layers.

The way the soil retains the K applied by the vinasse is very dependant on the soil CEC. Consequently, the clay and organic matter contents in the soil significantly contribute to the degree of leaching (Ribeiro et al. 2014). Thus, soils with low CEC present difficulty in retaining the applied K; therefore, leaching of this element becomes a problem for sandy soils (Mendes et al. 2016).

Simulation models help understand how processes occur in the soil related to solute displacement and tools applicable to environmental impact minimisation studies. It is essential to successfully model and simulating the equations that predict the displacement of solutes in the soil to determine better the transport parameters that influence the soil-solute relationship. The most relevant parameters obtained are pore water velocity, diffusion-dispersion coefficients, and retardation factor (Ribeiro et al. 2014). Given the above, this work aims to evaluate the fate and transport of Potassium ion (K^+), applied via vinasse, in a representative soil of the sugarcane zone (dystrophic Yellow Ultisol) of the Pernambuco State, Brazil. Potassium transport is determined by miscible displacement at fully saturated laboratory columns, and transport parameters are estimated using the CXTFIT programme.

2. MATERIALS AND METHODS

2.1 Soil

The soil of the study was collected in an area of a mill already fertigated with vinasse in different points (7°48'0.54"S and 35°0'18.45"W), being a dystrophic Yellow Ultisol - half slope (YUd), grown with sugarcane.

Ten soil samples were randomly collected in the study area to form a compositae sample in the 0-20 cm surface layer. The soil samples were stored in plastic bags, identified, and taken to the Soil Contamination Assessment Laboratory - LACS/UFPE. The soil was dried in a covered and airy place, then it was break up and passed through a 2 mm mesh sieve. This material was stored in a plastic bag and used for chemical and physical characterisation (Teixeira et al. 2017) and column assays.

2.2 Vinasse

Vinasse was collected in a tank of vinasse diluted at the proportion of 1:3 (vinasse:water). In the laboratory, the vinasse was subjected to physicochemical characterisation in pH metre, electrical conductivity (EC) metre, and flame photometer, with three replicates for each procedure. The characterisation of potassium was according to the Brazilian Norm 13805 (ABNT 1997).

2.3 Assays in soil columns

Potassium transport parameters were obtained from miscible displacement composed of three soil columns under saturation condition with 20.5 cm high and 5 cm diameter glass columns, filled with an average of 554.76 g of disturbed soil for each column, a twelve-channel peristaltic pump (ISMATEC), solute reservoirs for: deionised water, Calcium Chloride ($CaCl_2$) 0.05 mol L^{-1}, used as a tracer, vinasse; a fraction collector (CF-2 Spectrum Chromatography), test tubes, precision electronic balance, conductivity metre, and flame photometer (Figure 1).

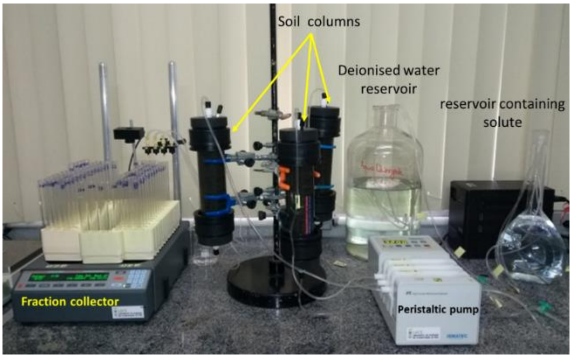

Figure 1. Experimental set-up for Potassium miscible displacement assays in saturated soil columns

The experiment consisted of displacing a specific volume of solute (V_0) of known concentration (C_0) in the three soil columns, previously saturated with deionised water. With the help of a peristaltic pump, the flow was injected with a constant average velocity.

As the solute infiltrates through the pores of the soil, it diffuses at varying velocities. The progression of the solute advance is followed by measuring the effluent concentration (C) over time. The evolution of the C/C_0 ratio as a function of the number of pore volumes of the collected effluent (V/V_0) provides the breakthrough curve. Then, and under the same conditions used for the tracer, the assays were performed with the vinasse.

Effluent solutions were analysed through the flame photometer to determine the potassium content, according to the procedure of ABNT-NBR 13805 (ABNT 1997).

Hydrodispersive parameters were estimated using the convection-dispersion (CD for tracer) and convection-dispersion at two sorption sites (CD-2S for vinasse) models using the CXTFIT 2.0 programme (Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments) developed by Toride; Leij; van Genuchten (1995).

2.3.1 Convection-Dispersion Model (CD)

The convection-dispersion equation (CD) for the one-dimensional transport of porous solutes subjected to adsorption in a homogeneous and undisturbed soil in the dimensionless form is given by:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{x} \qquad (1)$$

where C is the concentration of the solute in the liquid phase [$M\ L^{-3}$], D is the hydrodynamic dispersion coefficient [$L^2\ T^{-1}$], t is time [T], x is the spatial coordinate [L], v is the mean velocity of solution [$L\ T^{-1}$], and R is the retardation factor given by:

$$R = 1 + \frac{\rho_d K_d}{\theta} \qquad (2)$$

where K_d is the distribution coefficient ($K_d = S/C$) representing the distributed concentrations between the liquid (C) and sorbed (S) phase [$M\ L^{-3}$], θ is the volumetric water content [$L^3\ L^{-3}$], and ρd is the dry bulk density [$M\ L^{-3}$].

2.3.2 CD-2 sorption sites model (CD-2S)

When the solute interacts with the matrix of the soil, this interaction may occur instantaneously or not, represented by a parameter f, which corresponds to the fraction of sorption sites for which equilibrium is instantaneous with the liquid and mobile phase, and (1-f) which corresponds to the fraction of sorption sites for which equilibrium only occurs over time (Van Genuchten and Wierenga 1986).

For the case of steady flow in a homogeneous soil, the transport of a solute whose sorption is linear in the dimensionless form is given by:

$$\beta R\frac{\partial C_1}{\partial T}+(1-f)R\frac{\partial C_2}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial Z^2}-\frac{\partial C_1}{\partial Z} \qquad (3)$$

$$(1-\beta)R\frac{\partial C_2}{\partial T}=\omega(C_1-C_2) \qquad (4)$$

where C_1 is the concentration at equilibrium site, C_2 is the nonequilibrium site concentration, β is the partition coefficient between the two sites, P is the Péclet number, ω is the Damkhöler's number, T is time, and Z = x/L is the dimensionless spatial coordinate.

With:

$$\beta=\frac{\theta+\rho_d fK_d}{\theta+\rho_d K_d} \qquad (5)$$

$$\omega=\frac{\alpha(1-\beta)RL}{v} \qquad (6)$$

The initial boundary condition for the non-equilibrium transport model is given by:

$$C_1(Z,0)=C_2(Z,0)=C_i(Z) \qquad (7)$$

Input Condition:

$$C_1(0,T)=C_0(T) \qquad (8)$$

The output condition given by:

$$\frac{\partial C_1}{\partial Z}(\infty,T)=0 \qquad (9)$$

3. RESULTS AND DISCUSSION

3.1 Physical attributes of soil

The sand, silt, and clay fractions were 86%, 5%, and 9%, respectively, classifying the YUd as Loamy Sand (Table 1). The sand fraction is predominant, with 859.1 g kg^{-1}, and the coarse sand is higher than the fine sand content, which indicates the resistance of the source material to the physical and chemical weathering agents, despite the climatic conditions in the region favouring this phenomenon. The clay content of only 9% and the high sand content demonstrates the soil's rudimentary development, which may be related to the mineralogical composition of the source material, where quartz is probably predominant, being a more resistant mineral. The low levels of silt (5%) and the silt/clay ratio (0.5%) are due to the high degree of weathering of the originating material.

YUd had a high dry bulk density (1.67 g cm^{-3}), as it is sandy soil. According to Salviano et al. (2017), sandy-textured soils have a low moisture and nutrient retention capacity and are therefore considered very fragile environments, and the total porosity (37%) is deemed to be low for agricultural purposes (less than 50%).

Table 1. Physical attributes of the dystrophic Yellow Ultisol under sugarcane crop.

Layer	Particle size composition					Textural Class	S/C	FS/TS	ρ_d	Dp	φ
	Sand			Silt	Clay						
	Coarse	Fine	Total								
--cm--	------------------g kg^{-1}------------------						-------%------		---g cm^{-3}--		-%-
0 - 20	525.2	333.9	859.1	47	93.9	Loamy sand	0.5	0.39	1.67	2.64	36.76

S/C: Silt/Clay ratio; FS/TS: Fine sand/Total sand ratio; ρ_d: dry bulk density; Dp: Particle density; φ: Total porosity.

3.2 Chemical attributes of soil

The pH value in soil water was 6.7, with a slightly acidic pH. This pH is in the ideal range for sugarcane cultivation, which is at slightly acidic levels around 6.5, and is also close to the optimum pH range for most crops, which goes from 5.8 to 6.5, for presenting higher nutrient availability (Figueiredo et al. 2013). The almost neutral pH in the 0 to 20 cm layer is due to vinasse fertigation and liming during soil preparation for the next crop. The pH in KCl was 5.7, lower than the water's pH value, leading to a negative ΔpH, demonstrating the predominance of negative charges in the soil. This result is explained by the fact that as soil pH rises, negative charges predominate on these surfaces by liming or fertigation, responsible for attracting cations (McCauley, Jones, and Olson-Rutz 2017).

Table 2. Chemical attributes of the dystrophic Yellow Ultisol from the northern forest of Pernambuco.

Layer	pH		ΔpH	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{3+}
	H_2O	KCl						
----cm----				----------------------cmol$_c$ dm^{-3}----------------------				
0-20	6.7	5.7	-1	3.3	0.8	0.07	0.06	0
Layer	**H+Al**	**SB**	**t**	**T**	**V**	**m**	**P**	**TOC**
----cm----	--------------cmol$_c$ dm^{-3}--------------				------%------		mg dm^{-3}	g kg^{-1}
0-20	0.6	4.23	4.23	4.83	87.6	0	100	8.2

SB: Sum of bases; t: Effective cation exchange capacity; T: Potential cation exchange capacity; V%: Base saturation; m: Aluminum saturation; P: Phosphorus; TOC: Total Organic Carbon

Among the exchangeable bases, Ca^{2+} presented the highest concentration in YUd with 3.3 cmol$_c$ dm^{-3}. This is due to the addition of this nutrient through liming, with the insertion of calcium carbonate ($CaCO_3$) and calcium oxide (CaO), and also available through chemical fertilisation. Although the Mg^{2+} content was relatively low, as shown in Table 2, this was considered adequate for most annual perennial and forage crops, since its concentration is greater than 0.5 cmol$_c$ dm^{-3} of soil (Gabriel et al. 2018). Tezotto et al. (2012) state that deficiency should not occur if the soil has a Mg^{2+} content close to 0.8 cmol$_c$ dm^{-3}, the same Mg^{2+} value found in YUd.

K^+ and Na^+ contents were the lowest in YUd with 0.07 and 0.06 cmol$_c$ dm^{-3} soil, respectively. Sodium (Na^+) was the one with the lowest value, which may be related to the composition of the source material and the high precipitation that assists in washing cations such as Na^+ and K^+.

Still observing Table 2, one finds that: i) The sum of bases (SB) presented a value of 4.23 cmol$_c$ dm^{-3} in YUd, being considered suitable for an Ultisol (Gonçalves and Martins 2016). ii) The effective cation exchange capacity (t) was equal to the sum of bases because there is no exchangeable Al^{3+} in the 0-20 cm soil layer. Thus, aluminium saturation (m) was also zero, with no aluminium toxicity problems for the crops. iii) Potential cation exchange capacity (T) presented a value of 4.83 cmol$_c$ dm^{-3}, which, as well as effective CEC, is considered a low value of CEC (Mafra et al. 2011). Low cation exchange capacity (CEC) is related to low soil clay concentration (less than 10 %). iv) Phosphorus (P) value was very high in YUd, with P content of 100 mg dm^{-3} of soil, three times higher than the ideal P level for the soil in sugarcane 33 mg dm^{-3}. This value can be explained by the phosphate chemical fertilisation and the sandy texture of the 0-20 cm layer, allowing higher phosphorus availability due to the lower clay concentration. v) The Total Organic Carbon (TOC) concentration of 8.2 g kg^{-1} is considered low for good soil fertility (Ribeiro Filho, Adams, and Murrieta 2013).

3.3 Vinasse

The potential of hydrogen (pH), electrical conductivity (EC), and K^+ content are shown in Table 3.

Table 3. Chemical characteristics of vinasse.

SOLUTE	pH	EC ($\mu s\ cm^{-1}$)	K^+ ($mg\ L^{-1}$)
Vinasse	4.93	2220	688

3.4 Tracer and K miscible displacement assays

To perform the potassium miscible displacement assays on saturated soil columns, they followed the protocol defined in Table 4.

Table 4. Parameters used in the tracer and potassium miscible displacement assays.

CONSTANT PARAMETERS			Column 1	Column 2	Column 3
r_{column}	2.5	cm	-	-	-
L_{column}	20.5	cm	-	-	-
A_{column}	19.635	cm^2	-	-	-
V_{column}	402.517	cm^3	-	-	-
ρ_d	1.416	$g\ cm^{-3}$	1.395	1.366	1.374
D_p	2.64	$g\ cm^{-3}$	-	-	-
M_{column}	554.76	g	561.34	549.67	553.25
time	7	min	82.67	83.78	82.87
Q	2.52	$mL\ min^{-1}$	2.30	2.32	2.33
θ_s	0.463	$cm^3\ cm^{-3}$	0.472	0.483	0.479
PV	186.62	cm^3	189.89	194.31	192.95

r: Radius of the column; L: Column length; A: Area of the column; V: Volume; D_p: Particle density; M: Mass per column; t: collection time per test tube measured in minutes; Q: Flow for each column; θ_s: Saturated water content; PV: Pore volumes.

Parameter values obtained experimentally from the miscible displacement assays with the tracer are shown in Table 5.

Table 5. Results of hydrodispersive parameters for the Calcium Chloride ($CaCl_2$, tracer) assay in the three soil columns.

Parameters	Column 1	Column 2	Column 3
D (cm^2 h^{-1})	55.62 ± 4.677	25.17 ± 0.981	26.32 ± 1.398
R [–]	1.28 ± 0.036	1.17 ± 0.008	1.31 ± 0.013
Pe [–]	5.48	11.96	11.56
λ (cm)	3.74	1.71	1.77
K_d (L kg^{-1})	---	0.06	0.11

D: hydrodynamic dispersion coefficient; R: Retardation factor; Pe: Peclet number; K_d: Partition coefficient.

($\bar{x} \pm s$): mean ± mean square error.

In the $CaCl_2$ tracer assays, it was observed that breakthrough curves are nearly symmetrical (Figure 2) and with retardation factor values (R) slightly higher than 1, indicating that Cl^- barely reacts with the soil matrix (Table 5) and, therefore, under the absence of transport-related physical nonequilibrium. Partition coefficients (K_d) for Cl^- presented values close to zero for columns 2 and 3 and null for column 1, indicating little interaction with the soil. This is expected of an assay with the tracer.

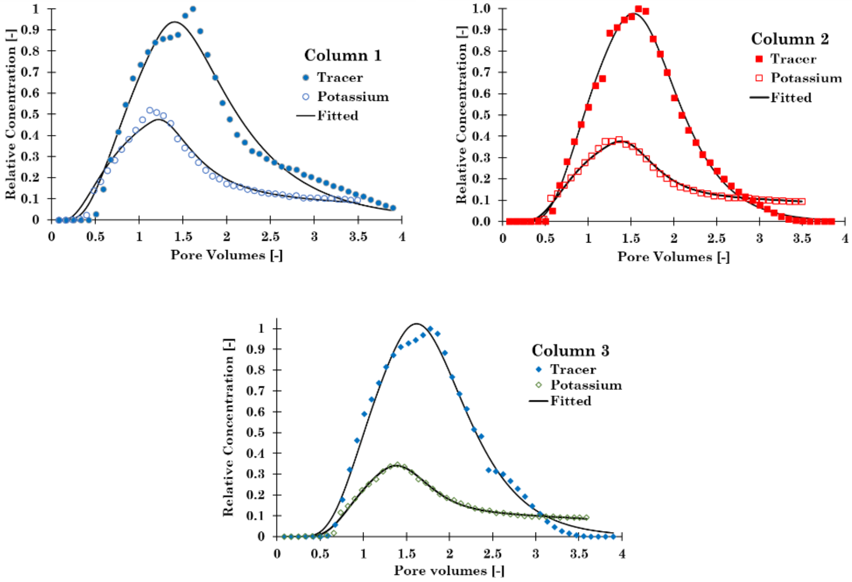

Figure 2. Breakthrough curves (experimental and fitted) of $CaCl_2$ (as a tracer) and Potassium (by vinasse) for dystrophic Yellow Ultisol (YUd).

The breakthrough curves for potassium transport (Figure 2) were delayed and asymmetrical with the posterior's prolongation to the peak. This type of behaviour can be explained by a series of processes that are grouped into two general classes related to transport (physical nonequilibrium) and sorption (chemical nonequilibrium) (Barizon et al. 2006). The potassium transport parameters were only due to the chemical nonequilibrium behaviour due to sorption.

Table 6 presents the results of the potassium hydrodispersive parameters estimated with the CD - two sorption sites model from the vinasse assays.

Table 6. Results of the potassium hydrodispersive parameters estimated from the CD - two sorption sites model for dystrophic Yellow Ultisol (YUd).

PARAMETERS	COLUMN 1	COLUMN 2	COLUMN 3
D (cm^2 h^{-1})	64.2 ± 16.93	27.0 ± 3.45	17.3 ± 1.69
R [-]	2.71 ± 0.172	3.75 ± 0.091	3.38 ± 0.213
β [-]	0.370 ± 0.037	0.267 ± 0.009	0.326 ± 0.026
ω [-]	0.0399 ± 0.0042	0.0582 ± 0.0015	0.05881 ± 0.0024
Pe [-]	4.44	10.58	16.92
K$_d$ (L kg^{-1})	0.58	0.97	0.83
***f* [-]**	2.26x10^{-5}	6.03x10^{-6}	4.19x10^{-2}
***α* (h^{-1})**	0.016	0.014	0.018
λ (cm)	4.62	1.94	1.21

D: Dispersion coefficient; R: Retardation factor; β: Dimensionless variable for partitioning nonequilibrium transport models; ω: Dimensionless mass transfer coefficient; Pe: Péclet number; K$_d$: Partition coefficient; *f*: Fraction of exchange sites assumed to be at equilibrium for the two-site model; α: First-order kinetic rate coefficient; λ: Dispersivity. $(\bar{x} \pm s)$: mean ± mean square error.

The values of dispersion coefficient (D) and dispersivity (λ) were higher for column 1, indicating a column more ready to solute dispersion in the soil matrix. The values found for Pe were like those of the tracer assays. In column 1, Pe presented a value of 4.44, being the lowest among the other columns, which means that in column 1 the dispersive process ($Pe < 10$) prevailed in the potassium ion transport behaviour (K^+). For columns 2 and 3, the convective behaviour prevailed with Pe values of 10.58 and 16.92, respectively.

The retardation factor (R) values for the potassium assays were higher than the tracer assays, increasing by 112%, 220%, and 158%, respectively, for columns 1, 2, and 3, showing that there was an interaction between the porous soil matrix and the ions potassium (K^+) from vinasse. In addition to R, the asymmetric curve shapes for both show chemical nonequilibrium due to two sorption sites, one at instantaneous equilibrium and the other following desorption kinetics (Figure 2). The chemical interaction processes between potassium and the soil in column 1 were inferior to the others, probably due to higher compaction during column assembly, favouring the formation of preferential flow pathways and the percolation velocity that could influence the retention process (N. F. Da Silva et al. 2012).

The values obtained in this work for the β parameter are low, pointing out chemical nonequilibrium due to potassium interaction with the soil matrix (Table 6). From the Damkhöler number (ω), the first-order kinetic rate coefficient was calculated. The highest resistance to mass transfer and slow chemical kinetics of potassium's reaction with the soil matrix was observed for column 2. For columns 1 and 3, the mass transfer resistance and slow chemical kinetics of potassium reaction with the soil matrix were slightly lower than in column 2.

According to Freitas et al. (2017), qualities such as organic matter present in vinasse promote improvement in soils, enabling nutrients such as K, especially in the 0-20 cm layer, where the soil has higher adsorption. However, the soil's physicochemical properties are altered in the presence of vinasse, especially the soil structure (Alfaro Soto et al. 2015). These alterations can act as a flocculant in the particles, compromising the particle size distribution, soil permeability, density, plasticity, among others, which can produce an imbalance in soil properties, causing interference in water dynamics (runoff, evapotranspiration, and infiltration), in addition to some contamination problems in soils, surface, and groundwater.

Therefore, while applying vinasse to sandy soil may contribute to increased soil fertility and reduced use of chemical fertilisers, soil characteristics should be respected when applying vinasse.

4. CONCLUSIONS

The transport and adsorption process by applying vinasse to the columns identified that the sandy soil retains potassium in a percentage proportional to the application time, which could not happen in times of rain since potassium is easily transported to deeper layers, which may or may not have the same interaction.

The CD-2 sorption site model represented the experimental data of potassium breakthrough curves for both columns, indicating the existence of chemical nonequilibrium, described by first-order sorption kinetics.

The evaluation model allowed to determine the sorption capacity and mobility of potassium ion in the soil, which showed that the vinasse dosage for a 0-20 cm layer should be carefully performed to avoid its leaching and consequent groundwater contamination.

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