

The Effect of Wetting and Drying Cycles on Potassium Release in Three Soil Orders

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ABSTRACT

This research was conducted to study the potassium release under ten wetting and drying cycles in three soil orders (Mollisols, Vertisols, and Aridisols) collected from three different locations (Sharya, Semeel, and Kanishrin) in Dohuk governorate in Iraqi-Kurdistan region by using Ca-resin capsules, and K^+ desorption (K_d) fitted to four model equations to choose the best equation to describe K^+ . The results of the experiments showed that flocculated water content wetting and drying cycles increased cumulative K-release from Ca-resin capsules until a tenth of the wetting-drying cycle. Potassium desorption according to the kinetic approach showed a significant effect of time on potassium desorption, and potassium desorption conformed to parabolic diffusion equations kinetics was the best equation to describe the K_d of potassium by using Ca-resin with a high coefficient of determination (R^2) and low standard error and the order of the equation in terms of their preference in describing the desorption process is as follows: 1 – Parabolic diffusion, 2 – Power function, 3 – Elovich equation, 4 – First-order. The apparent desorption rate coefficient for the parabolic diffusion equation ranged from 0.1084–0.0877–0.1040 $\text{cmol kg}^{-1}\cdot\text{day}^{-1}$ from Mollisols, Vertisols, and Aridisols respectively. The rate coefficient K^+ desorption according to the parabolic diffusion equation had a significant and positive correlation with SO_4^{2-} , K^+ , T- CaCO_3 , HCO_3^- , CEC, and Ca^{2+} but negatively significant correlated with EC and active CaCO_3 .

Keywords: potassium, release of potassium, soil orders, kinetics models, wetting and drying.

INTRODUCTION

For all plants, potassium is an essential nutrient (Mengel et al., 2001, White, 2003). A crucial macronutrient for living systems is potassium (K^+) (Hasanuzzaman et al., 2018). According to Johnston and Goulding (1990), K^+ in the soil can be divided into four fractions: soil soluble, exchangeable, non-exchangeable, and mineral K^+ . According to Kruuss (2003), the availability of soluble and exchangeable K^+ in soils is constrained by fertilizer management, soil texture, clay minerals, fertilization rate, and moisture content (Samadi, 2006, Simonsson, et al., 2007). Up to 57% of the applied potassium might be adsorbed by soil colloids, depending on the quantity and kind of clay minerals (Shanwall and Dahiya, 2006). Kinetic and thermodynamic factors influence how much

K^+ is adsorbed on clay particles (Du, 2004). To forecast the rate at which K^+ fertilizer is given to soils and effectively formulate K^+ fertilizer recommendations, one must be aware of the reaction rates between the solution and exchangeable phases of soil K^+ (Sparkes et al., 1980). The Elovich equation (Martin and Sparks 1983), the power function (Havlin and Westfall, 1985), the first order (Srinivasarao et al. 1998), and the parabolic diffusion (Sharma and Swami 2000) are some examples of kinetic equations that have been used to examine the release of non-exchangeable K^+ . First-order kinetics and the parabolic diffusion law were demonstrated to agree with the kinetics of K^+ desorption in heterogeneous soil systems (Sivasubramanim and Talibudeen, 1972). In their 1982 paper, Sparks and Rehcigl described fast exchange kinetics at external planar sites, slow

exchange kinetics at inner lattice exchange sites, and intermediate exchange kinetics at inner lattice edge sites. According to Mehmedany (1999) and Mam Rasul (2008), the optimum equation to describe the reaction rate of K^+ desorption from the governorates of Duhok and Sulaimani is a first-order equation (Kurdistan region).

The effect of wetting and drying cycles on K^+ fixation is well known; depending on the types and ratios of soil minerals, the amount of labile K^+ , and temperature, wetting and drying cycles can either encourage fixation or release (Betsh and Thomas, 1985). Additionally, it has been noted that soil moisture significantly impacts on the amount of potassium released and that drying and wetting limit the availability of K^+ for plants due to an increase in the K^+ fixation capacity of clay minerals (Sparks, 2001). According to Badraoui and Bloom (1989) and Assimakopoulos et al. (1994), the process of successive wetting and drying and the intensity of washing to the depths of the soil speed up the release of potassium. Hydration also causes the crystalline layers of the minerals to expand, which increases the amount of potassium liberated.

The rate at which the non-exchangeable part of K^+ is liberated into exchangeable and soluble forms is the most crucial factor in K^+ transformation in soil. The addition and removal of K^+ from soils are the two key mechanisms that determine the kinetic and equilibrium response between the forms of K^+ in soil. The addition of K^+ can be broken down into two primary components: the release of K^+ from soil minerals and organic matter, and soil fertilization. In contrast, the removal of K^+ from soils can be attributed to leaching and K^+ uptake by plants and microorganisms (Wada and Kakuto, 1993).

To examine the desorption and release kinetics of K^+ , a variety of models and methods have been used. These include batch and miscible displacement procedures (Sparks et al., 1980), H^+ resin (Martine and Sparks, 1983), Ca^{2+} – resin (Goulding, 1984), and Na TPB has been used as a K^+ sink (Cox and Joern, 1997). The exchangeable K^+ of Kurdistan soil is high at 0.64 to 1.99 $cmolc \cdot kg^{-1}$, especially in the cultivated layer. The rate and the amount of the release of non-exchangeable to exchangeable and soluble K^+ are principally dependent on the level of K^+ in the soil solution (Al-Zubaidi, 2003). So, this researcher was to find the most accurate mathematical model to represent K^+ release kinetics in the investigated

soils: and determine the K^+ release kinetics and their relationship with soil parameters in various soil orders.

MATERIALS AND METHODS

Three soil samples were taken from 3 soil orders (Mollisols, Vertisols, Aridisols,) from Sharya, Semeel, and Kanishreen locations respectively in Dohuk governorate in the Kurdistan region, Iraq to study the kinetics of K^+ desorption. The soil samples were air-dried and ground to pass through a 2 mm sieve for some chemical and physical analysis.

Physical and chemical properties of soils

The soil particle size distribution was determined by using the hydrometer (Ryan et al., 2001). The pH of soil extracts (1:2) was measured by the use of a pH meter model (Rowell, 1996). Electrical conductivity (EC) was measured for the soil saturation extract with EC-meter, in (1:2 soil: water) suspension with a conductivity meter and expressed as $dS m^{-1}$ at 25 °C (Robbins and Wiegand, 1990). Organic matter (OM) was determined by the dichromate oxidation procedure (Nelson and Sommers, 1986). soluble CO_3 , HCO_3 and, Cl^- according to (Estefan et al., 2013), and $Ca^{2+} + Mg^{2+}$, by titration methods (Rowell, 1996), Na^+ and K^+ by flame photometer (Estefan et al., 2013). Sulfate SO_4^{2-} was calculated from the difference between the total equivalents of dissolved cations and anions (Page et al., 1982). Cation exchange capacity (CEC) determined by using a flame photometer was obtained by saturation with 1M ammonium acetate (NH_4OAc) at pH 8.2 as an extraction solution (Summer and Miller, 1996). Total carbonate was done by treating a known weight of soil with hydrochloric acid (1N) with Calcimeter equipment (Loeppert and Suarez, 1996). Active calcium carbonate was determined by adding (0.2 M) ammonium oxalate to 2.5 g of soil and shaking to precipitate calcium oxalate and the excess of ammonium oxalate was determined by titration with potassium permanganate according to Kozhekov and Yakovoleva (1977).

Preparation of calcium-saturated resins

Put 500 grams of resin saturated with hydrogen in a plastic flask, add 2 liters of calcium

chloride solution (222 mg of CaCl_2 in 2 liters of distilling water) with shaking, leave for 72 hours, and filter then washed with deionized water to remove the Cl^- ions. The wet resin was spread on a filter paper and then leave the resin to dry, 5 g of resin was placed in T-shaped polyester fabrics.

Kinetics of K^+ Desorption Studies:

The kinetics of K^+ release was studied by (Lopez-Pineiro and Garcia Navarro 1997). five grams of Ca^{2+} resins capsules in T-shaped polyester fabrics and put 1 of each fabric containing Ca^{2+} resin under the ten soil samples in pots containing 1 kg of soil with similar depth for each soil order by three replicates. Irrigate the soil samples to 100% saturation percent (SP), after one day, or removing the first Ca^{2+} resins fabrics in pots for each soil, then allow the soil samples to dry for about 7 days, repeat this process for 10 dry-wet cycles, and record the time for each cycle. In the soil, desorption processes occur between Ca^{2+} resins and the K^+ ions in the soil solution, the extract the solution, and desorbed K^+ was determined by flame photometer. The release of K with time was fitted to the following equations:

First-order equation:

$$\ln (Ct/C_0) = K_d t \quad (1)$$

where: K_d – desorption rate coefficient of potassium;

Ct – amount of desorbed potassium at time t ($\text{cmol} \cdot \text{kg}^{-1} \cdot \text{soil time}^{-1}$);

C_0 – amount of desorbed potassium at equilibrium ($\text{cmol} \cdot \text{kg}^{-1} \cdot \text{soil time}^{-1}$).

Parabolic equation:

$$Ct = C_0 + K_d t^{1/2} \quad (2)$$

where: Ct – the amount of K^+ desorbed at times;

C_0 – the amount of desorbed K^+ at equilibrium;

K_d – the overall diffusion coefficient;

t – the time^{-1/2} in days.

Elovich equation:

$$Ct = 1/K \ln (C_0 K) - 1/K \ln t \quad (3)$$

Plotting Ct versus the term of the duration of the extraction ($\ln t$) the Elovich equation will be a straight line with the slop ($1/K$) and logarithmic intercept ($1/K \ln(C_0 K)$), the slop of the straight line was expressed for the rate coefficient of desorption of K^+ .

Power function equation

$$\ln Ct = \ln C_0 + k \ln t \quad (4)$$

where: Ct – the amount of K desorbed at time t^{-1} .

The best equations used to describe the kinetics of K desorption were evaluated by comparing the linear coefficient of determination (R^2) and the standard error (SE) of the estimate.

RESULTS AND DISCUSSION

Soil properties

The important physical and chemical characteristics of the soils are presented in Table 1. The studied soils had different contents of sand, silt, and clay size fractions. The low value of sand content and the high value of clay content were observed in Semeel soil (Vertisols), on the other hand, the high value of sand content and the low value of clay content were observed in Kanishreen soil (Aridisols). The soil pH varied from (7.32 to 7.63), and the electrical conductivity (EC) of soils was (0.302, 0.390, 0.279 $\text{dS} \cdot \text{m}^{-1}$) in Mollisols, Vertisols, and Aridisols respectively. The low amounts of Ca^{2+} , Mg^{2+} , and Na^+ reported could be due to the examined soils' low electrical conductivity (Warman and Termer 2005; Egbuchua 2007). Low values of cation exchange capacity were observed in Semeel soil (Vertisols), these could come from the soil's exchangeable bases washing out (Olatunji et al. 2007). The high active CaCO_3 found in Vertisols was 105 $\text{g} \cdot \text{kg}^{-1}$ soil, but the low quantity showed in Mollisols (65 $\text{g} \cdot \text{kg}^{-1}$ soil), while the range of organic matter from 12 to 24.7 $\text{g} \cdot \text{kg}^{-1}$ soil, the high amount in Mollisols but the low amount showed in Aridisol.

Effect of wetting-drying on potassium desorption

The effect of the drying and wetting ten times showed desorption of K^+ at the first time was high and decreased after two successions and was different between the three soil orders [Table 2, Figure 1] it may be due to K^+ content, quantity and quality of clay minerals, CEC, CaCO_3 and organic matter in the soil. This appears to explain the release of K from soils after drying because the degree of rotation of weathered soil minerals, such as micas, may change when the soil is dried.

Table 1. Some physical and chemical properties of soil were studied

Soil properties		Soil orders and location		
		Sharya	Semeel	Kanishreen
		Mollisols	Vertisols	Aridisols
Particle size distribution (PSD) g kg ⁻¹	Sand	149	99	474
	Silt	395	395	220
	Clay	456	506	306
Texture class		Clay	Silty clay	Sandy clay loam
pH		7.32	7.32	7.63
EC _{e25} dS m ⁻¹		0.30	0.39	0.28
Soluble cation Meq/L	Ca ²⁺	1.90	1.20	2.70
	Mg ²⁺	0.90	0.80	0.70
	Na ⁺	1.37	0.50	0.43
	K ⁺	0.18	0.10	0.13
Soluble anions Meq/L	CO ₃ ²⁻	-	-	-
	HCO ₃ ⁻	1.20	0.60	1.50
	Cl ⁻	1.00	1.00	1.00
	SO ₄ ²⁻	2.15	1.00	1.16
CaCO ₃ g kg ⁻¹ soil	Total	241.38	140.24	289.40
	Active	65	105	90
Organic matter (O.M) g kg ⁻¹ soil		24.70	17.10	12
Cation Exchange Capacity (CEC) cmol·kg ⁻¹		39.97	25.28	28.55

Table 2. Effect of wetting and drying cycles on the release of potassium

Wetting and drying cycle (time/days)	Desorption of potassium by using Ca ²⁺ – resin (mg K ⁺ ·kg ⁻¹)			Accumulation of K ⁺ desorption mg K ⁺ ·kg ⁻¹		
	Soil orders			Soil orders		
	Mollisols	Vertisols	Aridisols	Mollisols	Vertisols	Aridisols
1	70.0	60.0	56.7	70.0	60.0	56.7
8	60.0	40.0	30.0	130.0	100.0	86.7
15	30.0	30.0	26.7	160.0	130.0	113.4
22	30.0	25.0	23.3	190.0	155.0	136.7
29	30.0	25.0	23.3	220.0	180.0	160.0
36	26.7	20.0	33.3	246.7	200.0	193.3
43	23.3	23.3	43.3	270.0	223.3	236.6
50	37.0	26.7	33.3	307.0	250.0	269.9
57	37.0	23.3	26.7	344.0	273.3	296.6
64	23.3	26.7	40.0	367.3	300.0	336.6
Total	367.3	300	336.6			

As a result, the K-O bond may change, and dehydration of interlayer cations may allow redistribution of interlayer cations because Ca²⁺ could now compete with K⁺ for wedge sites (Mouhamad et al., 2016). Various soil characteristics in different soil orders, such as soil texture and clay mineralogy may influence how quickly K⁺ is released from these soils (Ghiri, et. al; 2011 a).

But the K⁺ desorption increased slightly after seven drying-wetting (43–50 days) from 23.3 to

37.0 mg·kg⁻¹ in Mollisols, while the K⁺ desorption increased after six drying-wetting (36–50) from 20 to 26.7 mg·kg⁻¹ in vertisols but in Aridisols the K⁺ desorption can frequently after five drying-wetting from 23.3 to 33.3 to 43.3 mg·kg⁻¹, this agrees with findings by Badraoui and Bloom (1989) and Assimakopoulos et al. (1994) that suggest it may be caused by the various expand modifications in the minerals structure of these soils.

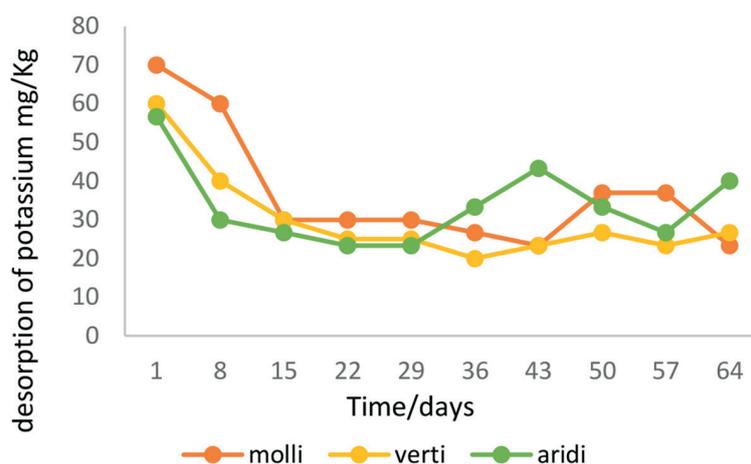


Figure 1. Release of potassium in three soil orders

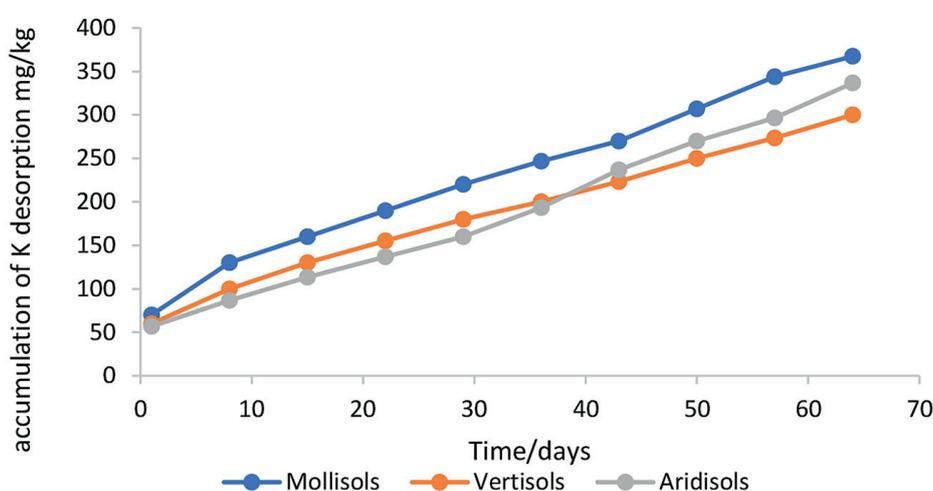


Figure 2. The relation between accumulative K⁺ desorption with time/days

The alternation of wetting and drying cycles greatly increased the release until the tenth cycle when the cumulative potassium reached 367.3 mg K⁺·kg⁻¹ in mollisols recorded the highest level of release of original potassium, while in vertisols it was 300 mg K⁺·kg⁻¹, and in aridisols, it was 336.6 mg K⁺·kg⁻¹ (Table 2), which is caused by the clay layers expanding and contracting alternately due to wetting and drying, and the release of the potassium part held between the layers (Sparks, 2000). Or that the variations in the labile potassium that takes place during the hydration and drying processes will, to a certain extent, reflect the gradual equilibrium of potassium from its different sources in the soil towards the release of potassium (Melean and Watson, 1985).

The results showed the accumulative potassium increase with increasing time from 1 day to 64 days of wetting-drying and ranged from (70.0 to 367.3, 60.0 to 300, and 56.7 to 336.6) mg·kg⁻¹ in

Table 3. Pearson Correlation coefficients between accumulative potassium desorption with soil properties

Soil properties	Accumulative of potassium
Sand	0.043
Silt	0.053
Clay	-0.129
pH	-0.018
EC	-0.660*
Ca ²⁺	0.379
Mg ²⁺	0.474
Na ⁺	0.82**
K ⁺	0.933**
HCO ₃ ⁻	0.567
SO ₄ ²⁻	0.937**
Total CaCO ₃	0.598
Active CaCO ₃	-0.933**
O.M	0.607
CEC	0.929**

* Correlation coefficients significant at p < 0.05.
 ** Correlation coefficients significant at p < 0.01.

Mollisols, Vertisols, and Aridisols respectively as illustrated in (Table 2, Figure 2). And showed two stages (Rapidly and Slowly) of the release of K^+ in studied soils due to the bond of K^+ to the soil. According to Talwo et al. (2018) and Akrawi and Esmail (2014), the amount of potassium released by successive extractions increased with time, there are two stages to potassium release: the first stage is characterized by the extraction of soluble and weakly bonded potassium (mostly exchangeable K^+), and the second stage is characterized by the release of strongly bonded potassium (mostly non-exchangeable K^+). In vertisols, smectites' tendency to swell made it simple for displaced cations to enter the interlayer area and release K^+ (Dhillon and Dhillon, 1990). Correlation between accumulative K^+ desorption with SO_4 , K, CEC, and Na was recorded (0.937**, 0.933**, 0.929**,

and 0.82**) respectively, but a negative correlation was found with active $CaCO_3$ (-0.933**) and EC (-0.660*) in (Table 3) Significant and positive relationships were found between cumulative K^+ release and silt content (Ghiri, et.al., 2011 b).

Equations describe potassium desorption

The Results of potassium desorption fitted to the First-order, parabolic diffusion equation, Elovich equation, and power function(Figure 3 and 4 all equations describe the reaction rate of K^+ desorption in the studied soils but choose the best equation depending on the highest value of the coefficient of determination (R^2) and the lowest value of the standard error of estimate (SE) (Sparks, 1992), the parabolic diffusion was the best equation described K^+ released in studied

Table 4. The determination coefficient (R^2) and standard error of estimate (SE) of various kinetic equations for potassium desorption in the studied soil

Soil orders	First-order equation		Parabolic diffusion equation		Elovich equation		Power function	
	SE	R^2	SE	R^2	SE	R^2	SE	R^2
Mollisols	0.173	0.896	0.043	0.973	0.112	0.814	0.104	0.963
Vertisols	0.158	0.911	0.034	0.974	0.092	0.809	0.117	0.951
Aridisols	0.115	0.965	0.072	0.921	0.138	0.707	0.205	0.887
Mean	0.148	0.924	0.049	0.956	0.114	0.776	0.142	0.934

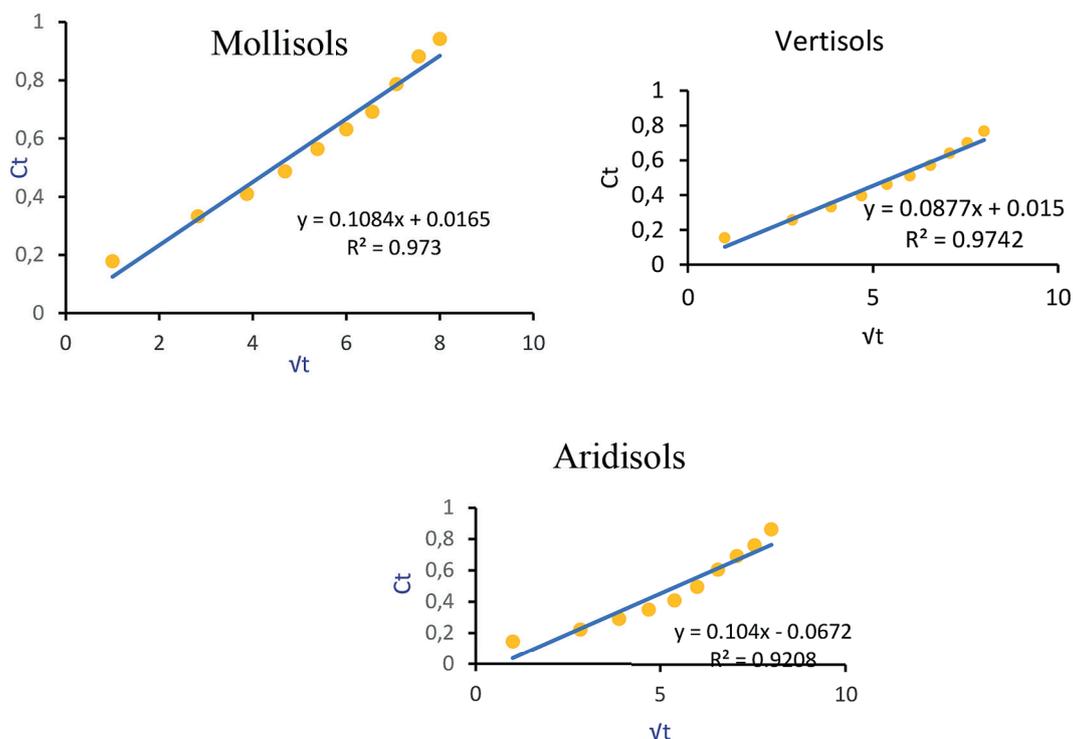


Figure 3. The cumulative K^+ desorption for studied soil by Ca^{2+} – resin according to the parabolic different equation from three soil orders

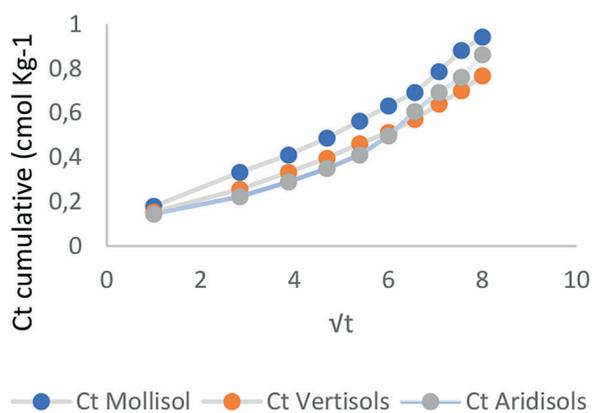


Figure 4. Parabolic diffusion equation kinetics of K^+ desorption by Ca^{2+} - resin from three soil orders

soils (Table 4) with $R^2 = 0.956$ and $SE = 0.049$. This result agreed with the finding by Dhillon and Dhillon (1990). These findings contrast with those made in the study by Taiwo et al. (2018), who found that the tested soils' potassium desorption followed first-order kinetic equations.

The rate coefficient of K^+ desorption (K_d) according to the parabolic diffusion equation

ranged between $(0.087\text{--}0.108 \text{ cmol kg}^{-1}\cdot\text{day}^{-1/2})$, the highest rate constant was for Shariya location soil (Mollisols), and the lowest for Semeel location soil (Vertisols) as shown in Table 5. While the rate coefficient K^+ desorption according to the power function equation ranged between 0.3864 and 0.4325 $\text{cmol kg}^{-1}\cdot\text{time}^{-1/2}$, the K_d was very low in the First-order equation. According to Al-Obaidi et al., (2015) the study found that variations in the physicochemical and mineralogical characteristics of the studied soil caused variations in K_d . The diffusion-controlled exchange was shown by the parabolic equation's superior performance in predicting the kinetics of K^+ release compared to the first-order kinetic equation (Dhillon and Dhillon, 1990).

The data in (Table 6) indicated that the positive correlation between the release of potassium rate K_d and soil properties according to the parabolic diffusion equation increased with increasing Ca^{2+} , K^+ , HCO_3^- , SO_4^{2-} , T- $CaCO_3$, and CEC was recorded (0.694*,0.865**, 0.837**, 0.900**, 0.862**, and 0.800*) respectively, but a negative

Table 5. Apparent desorption rate coefficient (K_d) according to kinetic equations in studied soils

Soil orders	First-order equation	Parabolic diffusion equation	Elovich equation	Power function
Mollisols	0.02267	0.1084	0.1757	0.3964
Vertisols	0.02247	0.08768	0.1415	0.3873
Aridisols	0.02673	0.1040	0.1615	0.4325
Mean	0.02395	0.1000	0.1596	0.4054

Table 6. Pearson's Correlation coefficients between desorption rate coefficients (K_d) of First-order, Parabolic diffusion, Elovich, and Power function with soil characteristics

Soil properties	K_d – First-order	K_d – Parabolic diffusion	K_d – Elovich	K_d – Power function
Sand	0.718*	0.418	0.220	0.987**
Silt	-0.720*	-0.333	-0.125	-0.977**
Clay	-0.708*	-0.491	-0.303	-0.985**
pH	0.735*	0.356	0.157	0.979**
EC	-0.551	-0.901**	-0.803**	-0.758*
Ca^{2+}	0.726*	0.694*	0.531	0.946**
Mg^{2+}	-0.569	0.311	0.440	-0.467
Na^{1+}	-0.287	0.604	0.761*	-0.413
K^{1+}	0.001	0.865**	0.950**	-0.015
HCO_3^-	0.616	0.837**	0.711*	0.840**
SO_4^{2-}	0.081	0.900**	0.961**	0.095
Total $CaCO_3$	0.605	0.862**	0.746*	0.819**
Active $CaCO_3$	0.001	-0.865**	-0.946**	0.000
O.M	-0.352	0.314	0.500	-0.658
CEC	-0.007	0.800*	0.909**	-0.141

* Correlation coefficients significant at $p < 0.05$.
 ** Correlation coefficients significant at $p < 0.01$.

correlation with EC and active CaCO_3 . In the power function equation highly positive significantly with sand, pH, Ca^{2+} , HCO_3^- , and T- CaCO_3 , while negatively significant with silt and clay fraction, and EC.

CONCLUSION

The result from this study showed that the cumulative potassium K^+ release of studied soils increased after the ten wetting-drying cycles. The cumulative potassium K^+ release in Mollisols soils was higher than in other soils because of the high cation exchange capacity, organic matter, and clay content up to a certain point which expanded and contracted alternately due to wetting and drying, and the release of the potassium to the equilibrium forms. The parabolic diffusion model was the best equation to describe K^+ release in all studied soils.

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