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Modeling the Release of Potassium in Selected Parent Materials in Akwa Ibom State, Nigeria

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Abstract

Potassium (K) is one of the major nutrient elements needed by plant in large quantity for growth and development. This study was carried out on three parent materials (sandstone, shale and alluvium soils) to determine the amount of potassium (K^+) released in soils and to find the best fitting model to describe K^+ release. Ten grams (10g) of soil was suspended in 20ml of 0.01m $Cacl_2$ at various K concentrations viz: 0, 50, 100, 150, and 200 mgL-K.. These were shaken at 25^{o}C, centrifuged and the concentration of K in the extract was determined. The soil samples were shaken repeatedly each time a fresh solution was added and the process repeated at 1, 2, 4, 8, 16, 32, 64 and 128 hrs. The physical and chemical properties of the soil were also determined. The result showed a variation in soil texture as in Sandstone (sandy loam with high sand content of 74.2%), Alluvium (sandy clay loam with high silt content of 13.0%) and Shale (sandy clay with high clay content of 33.4%). The pH of the soil was moderate; values ranged from 5.0 to 5.4. Salt levels were low: varying from Shale (0.02dsm^{-1}) < Sandstone (0.07 dms^{-1}) < Alluvium (0.08dms^{-1}). Organic matter was moderate varying from Sandstone (4.8gkg^{-1},) Alluvium > (4.2 gkg^{-1}) > Shale (3.4 gkg-1). Nitrogen was low, available phosphorous was moderate, varying from Sandstone (22.0 mgkg^{-1}) > Alluvium (10.5 mgkg^{-1}) > Shale (8.7 mgkg^{-1}). The most fertile soils indicated by base saturation varied as follows: Shale (86.6%) > Sandstone (80.6%) > Alluvium (65.2%). Results also showed an increased rate of K released with the concentration of K added and the extraction hours. The concentration of K released based on the different models were: Shale (0.106 mgkg^{-1}) > Sandstone (0.040 mgkg^{-1}) >Alluvium (0.027 mgkg^{-1}) for parabolic diffusion model; Alluvium (3.119 mgkg^{-1}) > Sandstone (2.853 mgkg^{-1}) > Shale (2.454 mgkg^{-1}) for power function model; Sandstone (3.654 mgkg^{-1}) > Alluvium (3.545 mgkg^{-1}) > Shale (2.916 mgkg^{-1}) for Eluvich model. The release of K were in these trend; Alluvium > Sand stone > Shale. For the parabolic diffusion R^2 = 0997 and for the Eluvich model R^2 = 0997. The two models were best fitted models in describing K release with the highest coefficient of determination. The two models are recommended in assessing K availability in the soils studied.

Keywords: Potassium, Kinetics release, Parent material, Parabolic diffusion, Power function and Elovich model

1.0 Introduction

Potassium (K) is one of the major nutrients that plants require for growth and development. Potassium appears in soil in several forms: structural (mineral), non-exchangeable (fixed or inaccessible), exchangeable, and water soluble (Dhahiwal *et al.*, 2006). The soil's K content is determined by the quantity of K incorporated in the solid phase. When crop removal reduces the K content in soil solution, it is gradually replaced by conserved K. According to research, plants use 10-20% of K, with the majority of it fixed in the soil at a rate of 70-90%. In acidic soils, insoluble hydrous oxides of Fe, Al, and Mn compete with K for adsorption sites, leaving the nutrient fixed. This causes widespread potassium deficiency, making it one of the most limiting crop nutrients. Nevertheless, the K that has been held in the soils is not completely lost, except by runoff or leaching. Umoh *et al.*, (2017) conducted a study to analyze the K recovery in different soils in South-eastern Nigeria and discovered substantial leaching of K in sandy soils. Many soil variables influence soil K release, including texture, organic matter, low pH, and the quantity and kind of clay (Umoh *et al.*, 2022).

The rates of soil K discharge into solution are critical to plant nutrition as well as crop production for their availability in soil to improve crop physiological efficiency (Ekwere *et al.*, 2023; Okon *et al.*, 2024). Many models have been employed to describe K release from 10 calcareous soils, including parabolic diffusion, power function, and simplified Elovich equations (Hosseinpur and Safari Sinegani, 2007; Samadi, 2010). They investigated the potential positive correlation between kinetic equation rate constants and garlic indices. They also discovered a substantial correlation between the Elovich and Zero-order equations' release rate constants and garlic indices. Umoh *et al.*, (2022) observed that the zero-order equation adequately characterized the K release in soils from Alluvium, Sandstone, and Shale; with the greatest R^2 values of 0.99, high K were accessible in alluvium soils. Soil K availability and release characteristics are estimated using extraction methods. Additionally, there is a scarcity of data on K release in the soils of Akwa Ibom, Nigeria. The goal of this study is to use the Elovich, power function, and parabolic diffusion models to measure K release from various soils as well as K status in different parent materials.

2.0 Materials and Methods

2.1 Location of the Study Area

The study was carried out in selected areas in Akwa Ibom State that represent various parent materials (Table 2.1). The state is bordered by Abia State to the north, Cross River State to the southeast, and the Atlantic Ocean to the south. It has an area of 8412 km2 and a shoreline of 129 km^2, covering the Akwa Ibom River Basin, the eastern section of the Lower Cross River Basin, and half of the Imo River Estuary. The climate of Akwa Ibom State depends on the movement in tropical discontinuity, which is the zone separating the warm humid maritime air mass with its associated south westerly wind from dry continental air mass (North-westerly winds). This wind gives rise to wet and dry seasons in the area. The rainfall pattern is bimodal and begins about March and ends in November with a little dry spell which gives rise to two maximum rainfall regimes with the heaviest rainfall in June for first rainfall and September for the second maximum. The annual rainfall in the wet season is usually heavy ranging from 2000 mm inland to over 3500 mm along the coast. The dry season starts from November and lasts till February, a period which coincides with overhead of the sun and high relative humidity of 75-90% (Peters *et al.*, 1989).

Shale soils (SH) are intermittently associated with the northern parts of the state. It consists mainly of medium to coarse grained sandstone which is restricted to the northern fringes of the state when they form ridges and hills. Sandstone soil (SS) is spread from the shoreline with a wide range of sandy and surface beaches to about 10 km inland where there is a recently deposited strip. They are deep, well drained, porous and heavily leached. Texturally they have sand to loamy soil on the surface. Agricultural potentials of these soils are very poor. They are marginally suitable for arable crops because of the fragile nature of the soils. Coconut and cashew tree crops have been known to thrive well. These soils are deep, poorly drained to very poorly drain; the texture varies widely from course to medium and fine loamy on the soil surface. They are suitable for production of short season crops like vegetables and grains during the short dry period. Soils in the area are generally acidic (Peters *et al.*, 1989).

2.2 Field Sampling

The soil samples were collected from three locations in Akwa Ibom State based on their parent material as shown in (Table 2.1). Samples were collected at a depth of 0-20cm with the aid of a soil auger. The soil samples were taken from ten points and bulked, from which a sub sample was obtained. These soils were air dried, crushed and sieved through a 2mm mesh and then used for laboratory analysis.

2.3 Physicochemical Analysis

The soil parameters listed below were determined as given by Udo *et al.* (2009). The Bouyoucos hydrometer method was used to determine particle size distribution, with sodium hexametaphosphate acting as a dispersant. A glass electrode pH meter was used to measure the soil pH at a soil-to-water ratio of 1:2.5. A conductivity bridge was used to assess electrical conductivity in an extract from a 1:2.5 soil-water suspension. Soil organic carbon was determined using the wet oxidation method, and the results were multiplied by a factor of 1.72 to yield organic matter. Total nitrogen was measured using the micro Kjeldahi technique. The Murphy and Riley method was used to determine the amount of available P in the soil following extraction with Bray P-1. The exchangeable cations in the soil were extracted using NH^4OAC. The extracts' K and Na were quantified using flame photometry, whereas Mg and Ca were assessed using atomic absorption spectrophotometry. The effective cation exchangeable capacity (ECEC) was calculated by summing the exchangeable cations. Base saturation (%) was determined by dividing the sum of basic cations (ECEC) by the total exchangeable bases (TEB) and multiplying by 100.

Table 2.1: Distribution of the Study Area

S/N	Parent Materials	Location	L.G.A	Vegetation	Crops Planted	Coordinate
1.	Shale	Mbiabong Ikot Udo	Ini	Rain Forest	Cassava, Maize, Oil Palm, Plantain	5^o 24'N 7^o 44' E
2.	Sand Stone	NtoNdang	Obot Akara	Rain Forest	Oil Palm, Cassavas, Yam	5^0.24'N 7^0.58'E
3.	Alluvium	Uta Ewa	Ikot Abasi	Rain Forest	Timber, Oil Palm, Timber	4^0.57'N, 7^0.57'E

Key: L.G.A-Local Government Area

2.4 Potassium (K^+) Release Study

Three (3) parent materials, five different rates of K (0, 50, 100, 150, 200 mg/L) at varying periods of 1, 2, 4, 8, 16, 32, 64 hours was used and replicated 3 times, a total of 360 samples were generated. A treatment solution containing 0, 50, 100, 150 and 200mg/litre of K prepared from KCl was added to 10g of soil sample. The treated soils were transferred into a 50ml centrifuge tube containing 10ml of 0.05M CaCl and were shaken for 1,2,4,8,16,32,64 and 128hrs. At the end of the equilibrium periods, the supernatants were decanted and filtered using a Whatman filter paper No. 42. Potassium in the extract was measured using flame photometry. Potassium released with time was fitted to the three (3) models as shown in Table 2.2

2.5 Statistical Analysis

The concentration of K was plotted against time. The K release kinetics was fitted using Elovich, power function and parabolic diffusion models (Table 2.2). The curve fitting was done using Microsoft Excel 2007 and linear regression was performed using SPSS version 19. The resulting models were compared based on R^2.

Table 2.2: Kinetic equations used in the study

Kinetic models	**Expression Form**
Parabolic diffusion	K_t = a+R x t $^{0.5}$
Power function	In K_t = In a+b Int
Elovich	K_t = a+ (1/B) Int

Key-K - amount of K (mg/kg) release at equilibrium, K_t - amount of K (mg/kg) released at time t (h), a– Intercept K_1, K, b and 1B = index of K release rates.

Source: Hosseinpur *et al*., 2012

3.0 Results and Discussion

3.1 Physical and Chemical Properties of the Studied Soil

The physical and chemical properties of the soils are presented in Table 3.1. Shale soils have the largest levels of sand (74.2%) and silt (12.4%). Shale soils had the lowest sand (54.4%) and silt (10.2%) concentration, while sandstone soils had the lowest clay level (13.4%). The variance in percentages of sand, silt, and clay reflects changes in the parent materials. A soil texture changes depending on whether it is sandstone (sandy loam), alluvium (sandy clay), or shale. These have an impact on water, nutrient retention, and leaching in soils (Umoh *et al.*, 2017). The soil pH in water ranges from 5.0 to 5.4 with the highest obtained in alluvium. The range is considered moderately acidic which is satisfactory for most crops (Okalebo *et al*., 2002). The electrical conductivity (EC) is low, and ranged from 0.02 to 0.08 dSm^{-1} indicating that the soil is salt free. Organic matter contents of the soils were above the critical level of 2gkg^{-1} proposed by Aduayi *et al*, (2002) for soils of Eastern Nigeria. The total nitrogen was low due to the poor drainage system. The order of abundance of exchangeable cations were Ca > Mg > K > Na and were adequate in the soils (Okalebo *et al*., 2002). The order of high to low fertility as indicated by the base saturation were as follows: shale (86.6%) > sandstone (80.6%) > alluvium (65.2%).

3.2 Release Kinetics of K from Soils

The potassium (K) release from soils of three parent materials obtained from the relationship between K extracted from the soils by 0.0lm $CaCl_2$ at varying concentration of K added and at different extraction time (h) are presented in Figure 3.1 (A - E). The letters A - E denote the amount of K added to the soil as: A =0, B =50, C =100, D=150 and E =200mgl^{-1}K.

Table 3.1: Some physical and chemical properties of the parent material

Soil Properties	Unit	Sand Stone	Alluvium	Shale
Sand	%	74.2	64.8	56.4
Silt	%	12.4	13.0	10.2
Clay	%	13.4	22.2	33.4
Texture		SL	SCL	SC
pH (H_2O)		5.0	5.4	5.2
EC	dsm^{-1}	0.07	0.08	0.02
OM	gkg^{-1}	4.8	4.2	3.4
Total N	gkg^{-1}	0.2	0.3	0.4
AV.P	mg gkg^{-1}	22.0	10.5	8.7
Ex. Ca	cmolkg^{-1}	6.0	3.8	4.7
Mg^1	cmolkg^{-1}	2.6	1.5	3.0
Na	cmolkg^{-1}	0.05	0.08	0.08
K	cmolkg^{-1}	0.1	0.2	0.3
EA	cmolkg^{-1}	2.1	3.0	1.25
ECEC	cmolkg^{-1}	8.75	5.58	8.08
Base Saturation	%	80.6	65.2	86.6

OM – Organic Matter, Av.P - Available Phosphorus, EA - Exchangeable acidity, ECEC – Effective Cation Exchange Capacity, SL – Sandy Loam, SCL - Sandy Clay Loam, SC – sandy clay, Total N - Total Nitrogen, Mg – Magnesium, Na – Sodium, pH (H_20) - pH in water

The figures are plots of the concentration of K release and extraction time (h) ranging from 1 to 128 hours. From figure 3.1A where no K was added, it shows a wide variation in the cumulative K released between soils. The highest concentration of K release was observed in alluvium while shale soil was lowest, the trend was alluvium >sandstone> shale parent materials. The concentration of K release in the soil increased with increasing rate of K added as well as the time of extraction. The differences in K release among the soil could be attributed to native K level in the parent materials in which the soils were formed and could also be attributed to the amount of clay and silt present in the soil. Sunday *et al*., (2020) reported that soil texture has a dominant effect on the release of potassium and that sandy soils exhibited higher K release in the soil than high clay soils.

The pattern of successive extraction of K from soils at different concentrations of K added is presented in Figure 3.1 (B - E). The concentration of K released after extraction time (h) differs significantly among soils. The release within one hour was significantly lower than the concentration observed at 128 hours. This is an indication that a considerable portion of non-exchangeable K was remaining in the soil; it also shows that unreleased non-exchangeable K will be released with time. This observation differs from the report of Datta (1993) who observed equilibrium in the 8th hour of extraction. This finding agreed with work of Dhaliwal *et al.*, (2006) who observed an increase in K release with increasing time. The amount of K release in the studied soil increased with increasing rates of K added. The amount released at 0mg L^{-1} of K, where no K was added was lower than where K was added as shown in figures 3.1(B -E). The result showed that the release was rapid (more K was released within a short period) when 0 to 50mgL^{-1}K was added, this was observed across soils. The fast release observed may be attributed to rapid dissolution of K^+ in the soils. Umoh *et al.,* (2022), observed a similar finding that K in solution is easily exchangeable. Sunday *et al.,* (2020) observed high release and leaching of K on sandy soils, attributing it to high concentration of Ca and Mg in soils which compete for adsorption sites, thus displacing K, which enters into the soil solutions. Addition of 100mgL^{-1}K to 200mgL^{-1}K did not record such sharp increase in K released. These indicate that proportions of the solution K were adsorbed on the surfaces of clay, which caused the slow release of K. Umoh *et al.,* (2017) observed a high fixation of K in soils developed from shale with high clay content. The trend was alluvium > sandstone > shale. The differences could be attributed to the nature of parent materials in which the soils originated as well as the amount of clay and silt content. The reason for the highest concentration of K released in alluvium soil could be that the soil is not well developed (young soil) with low clay content, and may have low charge density which is easily released while shale is well developed with layer silicate which could trap the element. The lower K release in shale soil could be attributed to the higher clay content and that proportions of the solution K were absorbed on the shale soil due to high clay content. This agrees with the finding of Mehdi *et al,* (2011) who reported that the soil properties (silt, clay and sand fractions) had significant effect on the release of K in soils. The release in sandstone could be attributed to the sandy nature of that parent material. These results are similar with the work reported by Umoh *et al.,* (2023), who observed a high recovery of K in alluvium and a high sorption of (K) in shale soils.

3.3 Potassium Release by Kinetic Models

Three mathematical models were used to assess the release of K from soils. Potassium release with time was calculated from the slope and the intercept from the graphs in figure 3.1, the coefficients of determination (R^2) was also obtained from the calculations. The parabolic diffusion reaction of K released is presented in Table 3.2. The amounts of K released in shale soil at 0, 50, 100, 150 and 200 mg L^{-1} of K added were 0.1509, 0.0444, 0.0294, 0.0277 and 0.0286 mg kg^{-1} respectively with mean of 0.106 mg kg^{-1}. Respective values for sandstone were 0.0888, 0.036, 0.0295, 0.0217 and 0.0252 mg kg^{-1}(mean 0.040 mg kg^{-1}) while respective values for alluvium soil were 0.0546, 0.0191, 0.0227, 0.0234 and 0.0165 mg kg^{-1} (mean 0.027 mg kg^{-1}). The R^2 values were 0.994 (shale) >0.998 (sandstone) >0.999 (alluvium). These values are low compared with the findings of Jalali and Zarabi (2006) and Mehdi *et al.,* (2011). The difference between K releases in soils may be attributed to the higher content of K as shown in Table 3.1

The power function of K release is presented in Table 3.3. The amount of K release in shale ranged from 1.4737 to 2.7681 mg kg^{-1} (mean 2.454mg kg^{-1}), 2.1984 to 3.1098 mg kg^{-1} (mean 2.853 mg kg^{-1}) in sandstone and 2.5381 to 3.3373 (mean 3.119 mg kg^{-1}) in alluvium. The mean R^2 values ranged from 0.912 to 0.922 mg kg^{-1} (mean 0.917mg kg^{-1}). The parameters of the Elovich equation for K release are presented in Table 3.4. The amount of K release in shale ranged from 2.78 to 2.8479 with (mean 2.916 mg kg^{-1}); 3.582 to 4.0229 (Mean 3.654 mgkg) in sandstone and 3.0343 to 3.9007 mg kg^{-1} (mean 3.545mg kg^{-1}) in alluvium. The mean R^2 values ranged from 0.994 to 0.999 mg kg^{-1} (mean 0.999 mg kg^{-1}). The mathematical models that best described the release of K at all concentrations using R^2 values are parabolic diffusion (0.997) and Elovich equation (0.997) which has a higher R^2 value than power function equation with the lowest R^2 values of 0.918.

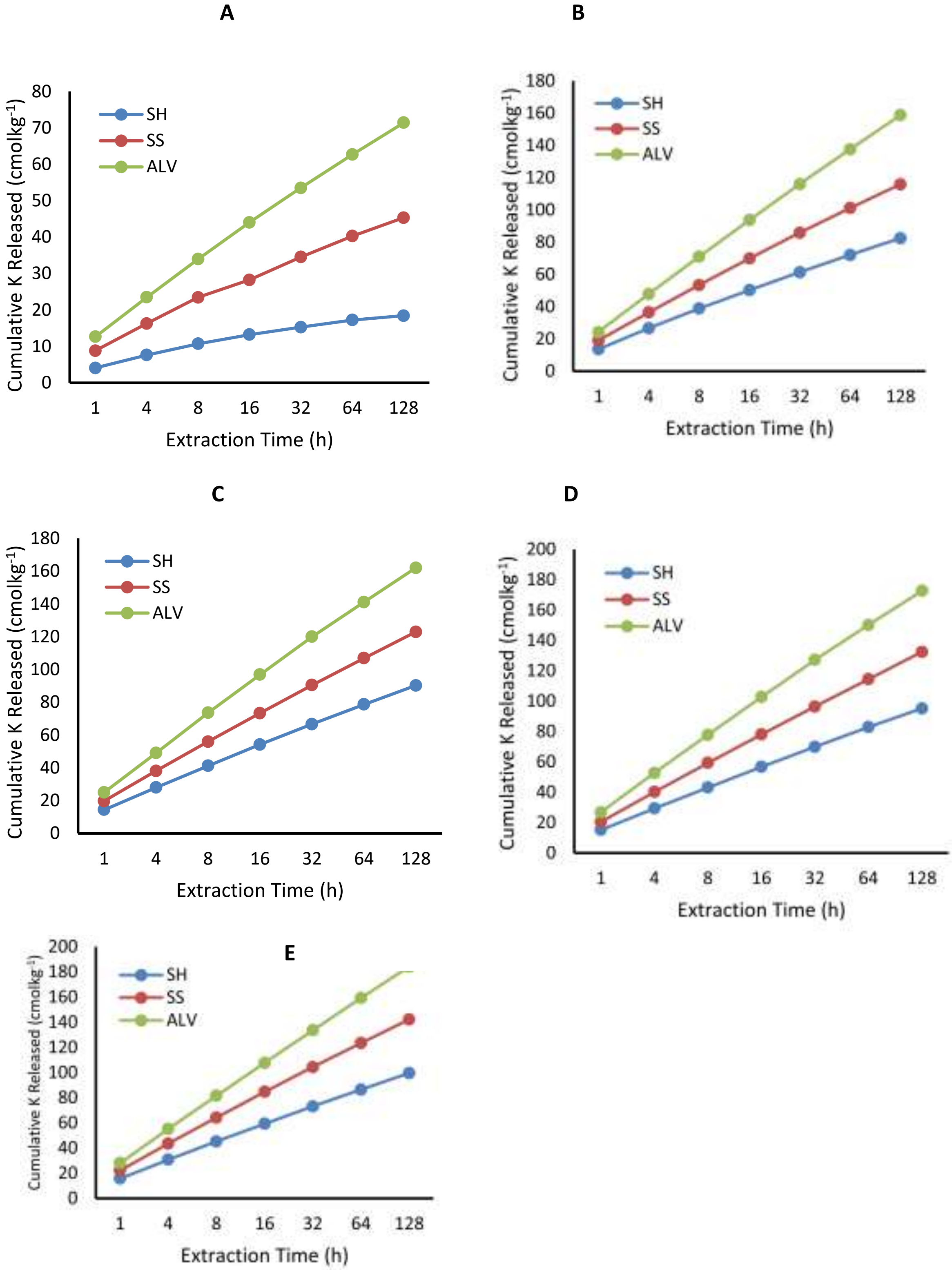

Figure 3.1: K release from soils of three parent materials at successive extractions when (A) 0 (B) 50 (C) 100 (D) 150 and (E) 200mgL^{-1} of KCl was added

Table 3.2: Slope, intercept and coefficient of determination for parabolic diffusion rate reaction of K release from soils of three parent materials (mg kg^{-1})

	0	50	100	150	200 MgL^{-1}	Mean	R^2 Mean
	←		mg kg^{-1}		→		
			P_1 (Shale)				
k	0.1299	0.1385	0.1403	0.1403	0.1400	0.1378	
a	0.1509	0.0444	0.0294	0.0277	0.0286	0.106	
R^2	0.975**	0.998**	0.999**	0.999**	0.999**	0.994**	0.994**
			P_2 (Sand Stone)				
k	0.1329	0.1395	0.14	0.1406	0.1406	0.139	
b	0.888	0.036	0.0295	0.0217	0.0252	0.040	
R^2	0.996**	0.999**	0.999**	0.999**	0.999**	0.998**	0.998**
			P_3 (Alluvium)				
k	0.1372	0.1413	0.1415	0.1411	0.1412	0.141	
b	0.0546	0.0191	0.0227	0.0234	0.0165	0.027	
R^2	0.999**	0.999**	0.999**	0.999**	0.999**	0.999**	0.999**
							(0.997**)

*** R^2 is highly significant ($P \leq 0.01$), K = the slope, a = Intercept, R^2 –Coefficient of determination, b = Intercept*

Table 3.3: Slope, intercept and coefficient of determination for power function rate of K release from soils of three parent materials

	0	50	100	150	200 (MgL^{-1})	Mean	R^2 Mean
	←		mg kg^{-1}		→		
			P_1(Shale)				
a	0.2337	0.2802	0.2882	0.2882	0.288	0.276	
b	1.4737	2.6335	2.6711	2.7221	2.7681	2.454	
R^2	0.876**	0.915**	0.921**	0.924**	0.922**	0.912**	0.912**
			P_2 (Sand Stone)				
a	0.2543	0.2836	0.2872	0.2919	0.2905	0.282	
b	2.1984	2.9497	2.9836	3.0253	3.1098	2.853	
R^2	0.914**	0.922**	0.924**	0.924**	0.922**	0.921**	0.921**
			P_3 (Alluvium)				
a	0.2722	0.2944	0.2935	0.2919	0.2947	0.289	
b	2.5381	3.195	3.2268	3.2965	3.3373	3.119	
R^2	0.923**	0.922**	0.919**	0.922**	0.926**	0.922**	0.922**
							(0.918)**

*** R^2 is highly significant ($P \leq 0.01$) , a = Slop, R^2 –Coefficient of determination, b = Intercept*

Table 3.4: Slope, intercept and coefficient of determination for Elovich rate of K release from soils of three parent materials

	0	50	100	150	200 (MgL^{-1})	Mean	R^2 Mean
	←		mg kg^{-1}		→		
			P_1 (Shale)				
a	2.3925	11.42	12.658	13.356	13.949	10.755	
B	2.78	3.6643	2.655	2.6343	2.8479	2.916	
R^2	0.975**	0.998**	0.999**	0.999**	0.999**	0.994**	0.994**
			P_2 (Sand Stone)				
K	6.0245	16.161	17.209	18.618	19.995	15.602	
A	4.0229	4.1686	3.6229	2.8729	3.5821	3.654	
R^2	0.996**	0.999**	0.999**	0.999**	0.999**	0.998**	0.998**
			P_3 (Alluvium)				
K	9.7991	22.435	22.919	24.353	26.022	21.106	
A	3.9007	3.0293	3.6736	4.0357	3.0343	3.545	
R^2	0.999**	0.999**	0.999**	0.999**	0.999**	0.999**	0.999** (0.997**)

*** R^2 is highly significant ($P \leq 0.01$), K = the slope, a = Intercept, R^2 –Coefficient of determination, b = Intercept*

4.0 Conclusion and Recommendation

This study was carried out on three parent materials (sandstone, shale and alluvium soils) to determine the nutrient status and amount of potassium (K^+) release in soils and to find the best fitting equations to describe the K^+ release in soils. The results revealed that soil pH organic matter, phosphorous, exchangeable Ca, K and Mg were moderate, base saturation values varied in the order: shale (86.65) > sandstone (80.6%) > alluvium (65.2%). Increase in amount of K added amounted to more K release in a shorter time. Parabolic and Elovich equations adequately described the reaction rate of K release in the studied soil with the higher R^2 values of 0.997. Information obtained from this study can help predict the supply potential of soil K and will also provide a suitable guide for fertilizer recommendation.

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