COMPARATIVE STUDIES OF FOUR PARAMETRIC MODELS FOR POTASSIUM ADSORPTION IN SOILS OF NYAMIRA COUNTY, KENYA

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ABSTRACT

Potassium is the third major nutrient after nitrogen and phosphorus. However, soil test for potassium often fail to reveal the true fertilizer demand in the field resulting to unreliable and inefficient fertililizer application to crops. This necessitated this field experiment to be carried out in soils of Nyamira county Kenya with an objective of fitting the experimental data into four parametric adsorption models and ascertain the most suitable adsorption isotherm which best fitted and described the studied soils. For adsorption studies 2.50 g soil samples were shaken with 25 ml 0.01 M $CaCl_2$ containing K concentration of 0, 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mg L^{-1} using potassium chloride for 24 hours at 25±1 °C to achieve equilibrium concentration. Langmuir, Freundlich, Temkin and Van Hauy adsorption models were applied to the data to check potassium adsorption in the soils. From the results, the physical-chemical properties of the soils revealed that the studied soils were acidic in nature with a mean pH of 5.19±0.2875. The soils were non-saline with electrical conductivity mean of 0.25±0.04475 mmhos/cm. The cation exchange capacity of the soil was 21.25±4.123 cmol/kg. Basic nutrients were low (Available K was 60.2±5.5408 mg/kg, available P (Olsen) was 9.71±0.056 mg/kg.and the organic carbon found to have a mean of 1.82±0.41%.) By application of the

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models, potassium adsorption data revealed that Freundlich model showed a good fit of K adsorption (r^2=0.957±0.021), then Van Hauy isotherm (r^2=0.923±0.021), followed by Temkin model (r^2=0.839±0.0316) and finally Langmuir model which did not fit well to the data (r^2=0.359±0.278).

Key words: *Potassium adsorption isotherms, Freundlich model, Van Hauy isotherm, Temkin model and Langmuir model.*

INTRODUCTION

Adsorption is the net accumulation of a chemical species at the surface between the solid and solution phase (sposito, 1987). Adsorption isotherm describes the equilibrium of the sorption of a material at the surface. It represents the amount of material bound at the surface (the sorbate) as a function of the material present in the solution. Sorption isotherms are often used as empirical models which do not make statements about the underlying mechanism and measured variables but use theoretical concepts of chemical equilibrium. An ideal model is usually applicable in a wide range of conditions without modification (Hannan, 2008). Also, is realistic when it conforms to accepted theories and predictive when applied to the most different conditions (Barrow and Bowden, 1987). Not many mathematical models possess such mentioned characteristics but some of the models possessing such properties include: Langmuir, Freundlich, Temkin and Van Hauy adsorption isotherm models.

Adsorption isotherms/models are used to predict adsorption phenomenon of various elements in soils. Constants calculated from the isotherms and interpretation based upon their meaning permit a sound theoretical approach to some of the problems of nutrient mobility and retention in the soil. Adsorption studies are often practical for essential elements such as P, K, S and Cu (Hunter, 1980). They often help to determine whether any of the applied nutrient react, fix or make complex with the soil. The approach involves fertilizer optima for enhancing crop productivity and understanding nutrient characteristics of the soil at experimental site. The approach provides safe levels of any one nutrient in the soil. This is true because it is adjusted in available pool of the soil level in which it is neither deficient nor toxic (Hunter, 1980). Researchers such as Pal et al 1999 have successfully used the approach to determine adsorption of potassium in the soils and Ederm et al 2004 have determined adsorption of Cu, Co, Zn and Mn.

K adsorption isotherms are part of the quantity-intensity approach (Neiderbudde, 1986) which can be used to evaluate the ability of soil to supply K to plants and to describe the exchange of K from soils by other ions such as Ca^{2+}.Traditionally, potassium adsorption capacities of soils have been determined using few parametric adsorption models. However, with better understanding of adsorption mechanisms and computational facilities has enabled researchers to use variety of existing models to evaluate their applicability on specific adsorbant-adsorbate systems (Vandenbruwane, 2007).The experimental results are adjusted and fitted to the models and validated through the significance of the coefficient of determination (R^2).

The objective of the research was to study potassium adsorption of the selected soil samples by fitting the experimental data into four parametric adsorption models and ascertain the most suitable adsorption isotherm which best fitted and described the studied soils.

MATERIALS AND METHODS

Experimental site

The experiment was carried out in Gachuba location in Nyamira County, Kenya. The soils are mainly classified as nitosols which are well drained (FAO-UNESCO, 1997). The area has a mean annual rainfall of 1700-1800 mm. due high population and pressure on land; all land is under cultivation with very small portion under pasture. The main crops grown in the area include: maize, beans, bananas, sugarcane, coffee, cassava, finger-millets, kales and cabbage.

Sampling

The study identified 5 locations of a farmland positioned within the same area and at close proximity. These sections have been consistently under cultivation. Five composite soil samples were collected from 0-30 cm depth. Grid sampling was employed due to uniform soil characteristics of the region in which samples were randomly collected from the locations. With the help of a soil auger 15-20 cores (a core is an individual boring or coring spot in a field) were collected from each grid at random. The cores were mixed thoroughly in a clean plastic pail to make composite soil samples. The bulk composite samples were air dried, ground, passed through a 2 mm sieve, packed in clean polythene bags, kept cool and were ready for use in the study.

Laboratory analysis

Physical-chemical parameters affecting soil fertility were analysed. The parameters included: soil pH and electrical conductivity (*EC*) of soil paste that was determined by electrical pH and conductivity meter respectively in a ratio of 1:2.5 soil to water. Total organic carbon was determined by Walkey Black rapid titration method. Phosphorus content was determined by Olsen method and calorimetric measurement. Nitrogen was determined by Kjeldal method. Potassium, were determined according to method described by Pratt (1965) and their concentration measured using flame photometer 410 Corning model.

Adsorption studies

For adsorption studies 2.50 g soil samples were shaken with 25 ml 0.01 M $CaCl_2$ containing K concentration of 0, 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mg L^{-1} using potassium chloride for 24 hours at 25±1 °C to achieve equilibrium concentration This process was repeated three times. After shaking, the solution was filtered through Whatman filter paper No. 42. After filtration, K concentration in the filtrate was measured using a flame photometer and adsorption isotherms constructed as per the method described by (Rowell, 1994). The amount of K adsorbed was determined by subtracting the equilibrium solution K concentration from the added K as shown in the equation below.

$\Delta K = (CK_i - CK_f) * (V / M)$

Where ΔK is the change of K in soil solution. Positive ΔK values indicate adsorption by the soil solid phase whereas negative values indicate desorption by the soil. CK_i and CK_f are the initial K concentration added and final equilibrium concentrations of K in solution respectively. V and M are the solution volume and mass of the soil used. The isotherms were obtained by adding a value equal to the amount of K desorbed in a solution containing an initial K concentration of 0 mg/L to the amount of K adsorbed/ desorbed in solutions containing various initial K concentrations. For fitting experimental data, the linearized forms of the equations are used as shown below:

Langmuir adsorption equation

$$\frac{C}{(X/m)} = \frac{1}{kb} + \frac{C}{b}$$

Where C is the equilibrium solution K concentration (mg L^{-1}), X / m is the mass of K adsorbed per unit mass of soil (mg Kg^{-1}), k is a constant related to bonding energy of K to the soil, and b is the maximum K adsorption capacity of the soil.

Temkin adsorption equation

The linearized form of the equation is shown in equation below.

$$\frac{X}{m} = a + bInC$$

Where X/m is the mass of K adsorbed per unit mass of soil (mg Kg^{-1}), C is equilibrium solution K concentration (mg L^{-1}), a is amount of K adsorbed of Temkin model (mg/Kg) and b buffering capacity of Temkin model constants obtained from the intercept and the slope respectively**.**

Freundlich adsorption equation

Freundlich isotherm model gives a closer description of the real adsorption phenomena in the soil. The un-linearised form of the equation is shown in equation below.

$$\frac{X}{m} = aC^b$$

By rearranging and log transforming the equation, the linearised form of the equation will be as shown in equation below and used for fitting experimental data.

$$log\left(\frac{X}{m}\right) = loga + blogC$$

Where X / m is the mass of K adsorbed per unit mass of soil (mg Kg^{-1}), C is the equilibrium solution K concentration (mg L^{-1}), a and b are constants obtained from the intercept and slope respectively.

Van Hauy adsorption equation

$$\frac{X}{m} = m + n\sqrt{C}$$

Where X / m is the mass of K adsorbed per unit mass of soil (mg Kg^{-1}), *C* is the equilibrium solution K concentration (mg L^{-1}), *m* and *n* Vay Hauy isotherm constant obtained from the intercept and slope respectively.

RESULTS AND DISCUSSIONS

Physical and chemical properties of the studied soil samples

Selected physical and chemical properties of the studied soils are shown in table 1 below. The studied soil samples were all loamy. They are all acidic with pH ranging from 4.81-5.61 and a mean of 5.19±0.2875. The amounts of soluble salts are low ranging from 0.20-0.31 and a mean of 0.25±0.04475. This means that the soils are non-saline. The cation exchange capacity of the soils ranged from 17.25-28.05 cmol/kg with a mean of 21.25±4.123 cmol/kg. This indicates that the soils can hold moderate amounts of nutrients. Basic nutrients were low. Available K ranged from 57-70 mg/kg with a mean of 60.2±5.5408mg/kg, available P (Olsen) ranged from 9.62-9.77 mg/kg with a mean of 9.71±0.056 mg/kg. the organic carbon ranged from 1.10-2.07 % with a mean of 1.82±0.41%.

Table 1. Selected properties of the studied soils, n = 5

Soil	Organic carbon %	Available P_{Olsen} mg/kg	Available K_{NH4OAC} mg/kg	CEC cmol/kg	pH	Electrical conductivity Mmhos/cm
1	2.03	9.70	70	28.05	5.20	0.28
2	1.87	9.73	57	19.40	4.81	0.20
3	1.10	9.73	59	19.80	5.10	0.24
4	2.03	9.62	57	21.75	5.23	0.22
5	2.07	9.77	58	17.25	5.61	0.31
Mean,	1.82±0.41	9.71±0.056	60.2±5.54	21.25±4.123	5.19±0.287	0.25±0.0447

Langmuir adsorption isotherm

The adsorption isotherms were examined according to the linear form of the equation. When adsorbed K potassium data was plotted in Langmuir adsorption isotherm by taking C/(x/m) against the equilibrium concentration a poor fit was obtained as indicated by low values of coefficient of determination (R^2) as shown in table 1 below. The coefficient of determination ranged from 0.006-0.743 and a mean of 0.359±0.278. The Langmuir adsorption isotherm could not fit well to the K sorption data of the soils under study. This might be due to the fact that the Langmuir model assumes homogeneity of sorption sites with a complete monolayer adsorption of solutes (Pal, *et al* 1999).

Table 1. Regression equations from Langmuir isotherms and coefficient of determination (R^2). n = 5

Soil sample	Langmuir equations	R^2
1	$y = -0.000X + 0.093$	0.743
2	$y = -3E - 05X + 0.072$	0.006
3	$y = -0.000X + 0.098$	0.399
4	$y = -0.000X + 0.078$	0.192
5	$y = -0.000X + 0.092$	0.454
Mean		0.359±0.278

Freundlich adsorption isotherms

Plotting log $(\frac{x}{m})$ against $logC$ showed a good fit with coefficient of determination (R^2) ranging from 0.927-0.985 and a mean of 0.957±0.021. The average values of Freundlich of coefficient of determination were greatest compared to Langmuir, temkin and van hauy (R^2) values. The high linear relationship might be due to reason that Freundlich model assumes unlimited adsorption sites of heterogeneous medium having a mixed mineralogy in soils (Hannan, 2008). The slopes which represent the freundlich K buffering capacity were found to be less than1.3. Freundlich slopes ranged from 1.079-1.27 L/Kg with a mean of 1.171±0.0736 L/Kg. The amount of K adsorbed on unspecific sites ranged from 4.977-11.092 mg/Kg.with a mean of 6.993±2.378 mg/kg

Table 2. Freundlich adsorption parameters, n = 5

sample	Freundlich equations	R^2	Bonding energy soil k L/kg	K buffering capacity mg /kg
1	$y = 1.19x + 0.817$	0.985	1.190	6.561
2	$y = 1.211x + 0.766$	0.927	1.211	5.834
3	$y = 1.27x + 0.697$	0.959	1.270	4.977
4	$y = 1.079x + 1.045$	0.947	1.079	11.091
5	$y = 1.195x + 0.813$	0.968	1.195	6.501
mean		0.957 ± 0.021	1.171 ± 0.0736	6.993 ± 2.378

Temkin adsorption isotherm

The temkin adsorption equations were obtained after plotting the $\frac{x}{m}$ againistInC. It was observed that the temkin equation showed a good fit compared to Langmuir equation but it is superiority was lesser than Freundlich and Van Hauy equations. The coefficient of determination ranged from 0.807-0.890 and amean of 0.839 ± 0.0316. Temkin buffering capacity (slope) was 0.001 ± 0.00 L/Kg for the studied soil samples.

Table 3. Temkin linear equations and coefficient of determination, n = 5

Sample 1	Temkin equations	R^2
1	$y = 0.001x + 2.892$	0.847
2	$y = 0.001x + 2.734$	0.827
3	$y = 0.001x + 2.885$	0.890
4	$y = 0.001x + 2.804$	0.826
5	$y = 0.001x + 2.556$	0.807
Mean		0.839 ± 0.0316

Van Hauy adsorption isotherms

Van Hauy adsorption isotherm was obtained by plotting adsorbed $\frac{x}{m}$ against$\sqrt{C}$. It was observed that Van Hauy equations showed a good fit compared Temkin and Langmuir but never outdid

Freundlich equations. It had coefficient of determination which ranged from 0.895-0.935 with a mean of 0.923±0.021.

Table 4. Van Hauy equations and coefficient of determination (R^2), n = 5

Sample	Van Hauy equations	R^2
1	$y = 0.004x + 4.023$	0.926
2	$y = 0.004x + 3.675$	0.910
3	$y = 0.004x + 3.922$	0.947
4	$y = 0.004x + 3.887$	0.895
5	$y = 0.004x + 4.098$	0.935
Mean		0.923±0.021

Conclusion

The adsorption isotherm showed closely related curves for the five soil samples due to uniform soil mineralogy and parent of the studied soil. Comparing the four equations, Freundlich, Van Hauy, Temkin and Langmuir equations fitted the data in that order respectively. Freundlich and Van Hauy provided the good fit for the data but the Freundlich equation was the best in describing the adsorption of the soils with average R^2 value of 0.957±0.021, followed by Van Hauy equation R^2=0.923±0.020, temkin equation R^2=0.0.0829±0.0316 and Langmuir equation R^2=0.359±0.278. Freundlich model fitted well to K adsorption due unlimited adsorption sites of heterogeneous medium having a mixed mineralogy in soils. Langmuir model assumes homogeneity of sorption sites with a complete monolayer adsorption of solutes hence might be reason for not fitting well to the adsorption data.

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