Agronomic Implication of the Competitive Adsorption between NH_4^+ and K^+ in a Selected Cocoa growing Soil in Nigeria

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ABSTRACT

Commonly used fertilizers among farmers in Nigeria come in compound form (N:P:K; 15:15:15). Usually, there are two main sources of nitrogen in compound fertilizer: nitrate N and ammonium N. The two nitrogen sources are combined in most compound fertilizers. This study was carried out to evaluate the possible impacts of chemical interactions between K^+ and NH_4^+ on potassium bioavailability in soil when fertilizers containing both cations are applied. Soil samples were collected from existing cocoa plantation and subsequently equilibrated in solution containing only potassium ions (20, 40, 60, 80 and 100 mg L^{-1}K) in a batch adsorption manner. Since the study was a comparative type, subsamples of the same soil were equilibrated in solution containing ammonium and potassium ions (20, 40, 60, 80 and 100 mg L^{-1}(K/NH_4). Result shows a 64.6, 35, 18, 18 and 14% reduction in K adsorption in soil treated with solutions containing ammonium and potassium when compared with soil treated with solution that contained only potassium. Among the various adsorption models tested, the Freundlich model gave the highest value of coefficient of determination R^2. The study showed that, application of N: P: K fertilizer that has NH_4^+ as its N source could result in the reduction of potassium storage capacity of the soil for plant use.

Keywords: Potassium, Ammonium, fertilizer, adsorption, cocoa

INTRODUCTION

Cocoa (*Theobroma cacao*) is the major cash crop that contributes to foreign earning in Nigeria. It is one of the most important tropical crops in West Africa. West Africa contributes 70% of the world's cocoa production (Wessel and Quist-Wessel, 2015). Currently, cocoa production in Nigeria is within 200,000 metric tonnes (Statista, 2016). In the past, Nigeria used to be one of the largest producers of cocoa in the world but her interest in the crop suffered a grave setback when the discovery of crude oil was made. Apart from the interference of crude oil commercialization on the nation's interest in cocoa production, there are other factors that have contributed to the downward trend in cocoa production in Nigeria. These include but not limited to: ageing of cocoa trees, ageing of farmers, pests and diseases and nutrients deficiency in soil.

In spite of the low soil fertility occasioned by continuous cocoa cultivation without nutrient replenishment, most cocoa farmers in Nigeria do not use fertilizer on cocoa (Ogunlade *et al* 2009). Most of them have the mindset that their plantations are usually enriched from the decay of annual leaf litter fall. On the contrary, Ogunlade and Iloyanomon (2009) showed that the quantity of leaf litter and their nutrient contents especially P, K and Ca were not sufficient to make up for the annual nutrient mining for cocoa beans

production. Production of 1000kg of cocoa beans removes about 20kg N, 41kg P and 10kg K from the soil (Omotoso1975, Aikpokpodion, 2010)

Potassium is one of the major nutrients required by cocoa. Significant role is played by potassium in enhancing crop quality. High level of available K improves the physical quality, disease resistance and shelf life of fruits and vegetables used for human consumption. The effect of K deficiency can cause reduced yield potential and quality long before visible symptoms appear. Plants depend upon potassium to regulate the opening and closing stomates. Proper functioning of stomates is essential for photosynthesis, water and nutrient transport and plant cooling. Potassium activates at least sixty different enzymes involved in plant growth. It also neutralizes various organic anions and other compounds within the plants helping to stabilize pH between 7 and 8 which is optimum for most enzyme reactions. Hence, the amount of K present in cell determines how many enzymes can be activated and the rate at which a given reaction can proceed.

Potassium is necessary for sugar transport. In plants sugar produced in photosynthesis is normally transported through the phloem to other parts of the plant for use and storage. Plant transport system uses ATP as energy. If K is inadequate, less ATP will be made available and the transport system will break down resulting into accumulation of photosynthates in the leaves which ultimately leads to reduction in photosynthesis. Normal development of energy storage organs such as cocoa beans is retarded.

Potassium plays key role in the transportation of water and nutrients in plant via the xylem. When K supply is reduced, translocation of nitrates, phosphate, calcium, magnesium and amino acids is depressed. Enzymes that participate in the transport of nutrients and water in plants are activated by K.

Every major step for the synthesis of protein in plant requires potassium. The "reading" of the genetic code in plant cells for protein production would be impossible without adequate potassium. When plants are deficient in potassium, proteins are not synthesized despite an abundance of available nitrogen. Instead, protein precursors such as amino acids, amides and nitrate accumulate.

Potassium is highly mobile in plant and translocated from the older to younger tissue. As a result, its deficiency symptoms usually occur first on the lower leaves of the plant and progresses towards the top as the severity of the deficiency increases (Tuma et al. 2004). The commonest visible deficiency symptom of K in plants is the yellow scorching or firing (chlorosis) along the leaf margin. In severe cases of potassium deficiency, the fired margin of the leaf may fall out. In the case of broad leaf crops like cacao, the entire leaf may shed resulting in premature defoliation of the crop. Potassium deficient crops grow slowly and have poorly developed root system (Prajatati and Modi, 2012). When potassium is insufficient in plant, winter- killing of the perennial crops can occur (Prajatati and Modi, 2012). Seeds from potassium deficient plants are small shriveled and are more susceptible to diseases. Fruit is often lacking in normal coloration and low in sugar contents.

In order to address the challenge of low productivity of cocoa as a result of non usage of fertilizer by farmers, the Federal government of Nigeria brought up several agricultural developmental programmes to sensitize and educate the farmers on the importance of fertilizer in cocoa production. In addition to sensitization and education, the government of Nigeria also went ahead to distribute compound fertilizer (N: P: K 15:15:15) to the farmers at subsidized rate. Consequently, most cocoa farmers have developed interest in the application of fertilizers on their farms.

In fertilizer formulation, the two common sources of N are ammonium (NH_4^+) and nitrate (NO_3^-). Either or both of the two compounds of nitrogen can be used by fertilizer manufacturers as nitrogen source. In most compound fertilizers available in Nigeria, both N sources are combined as NH_4NO_3. When inorganic fertilizer containing NH_4 is applied to the soil, soil bacteria convert it to nitrite followed by oxidation of

nitrite to nitrate under favorable environmental conditions. But if the soil condition becomes unsuitable for the chemical transformation to take place, abundance of NH_4^+ in soil solution will generate chemical interaction between NH_4^+ and K^+ on adsorption sites of the soil. The two chemical species are monovalent cations and have similar chemical properties. Hence, the chemical interaction could ultimately impair the bioavailability of either or both of the nutrients. The aim of this study is to evaluate the impact of adsorption competition between NH_4^+ and K^+ on potassium adsorption in cocoa growing soil.

MATERIALS AND METHODS

Soil samples were collected with soil auger under existing cocoa plantation at Ikom (5°52` N, 8°48`E) in Cross River State, Nigeria. The sampling was done at several points within the plantation at a depth of 0-15cm using soil auger. All the obtained samples were bulked and thoroughly mixed. The composite sample was air-dried, sieved and processed according to standard procedure (A.O.A.C, 2003). Soil pH was measured in 1:1 soil: water ratio, nitrogen was determined using Kjeldahl digestion method (AOAC, 2003) while particle size was determined by hydrometer method (Bouyoucos, 1951). Available phosphorus was determined by Bray 1 method (Bray & Kurtz, 1945), organic carbon was determined by the wet digestion dichromate acid-oxidation method (Olsen and Sommers, 1982). Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were extracted with 1N ammonium acetate buffered at pH 7.0 (Thomas, 1982). Exchangeable Ca, Mg, Zn and Mn in the extract were quantified using Bulk Scientific Atomic Absorption Spectrophotometer while K and Na were determined with Jenway PFP 7 flame photometer. Exchangeable acidity was determined by extracting the soil samples with 1N KCl and titrating the extract with 0.05 NaOH using phenolphthalein indicator (Mcclean, 1965).

Effective CEC was determined by summation method.

Solution preparation

For the Batch adsorption process, two different stock solutions were prepared. One was a solution containing only K^+ while the second solution contained both K^+ and NH_4^+. The stock solution of 1000mg $L^{-1}(K^+)$ was prepared from analytical grade KCl while the stock solution of 1000 mg $L^{-1}(K^+/NH_4^+)$ was prepared by weighing appropriate amount of NH_4Cl and KCl into 1L volumetric flask, dissolved and made up to mark with deionized water. The content and solvent were well mixed to attain homogeneous solution. From the stock solution of 1000 mg K L^{-1}, solutions of different concentrations (20, 40, 60, 80 and 100mg $L^{-1}(K^+)$ were prepared by introducing appropriate amount of the stock solution into respective 1L volumetric flask and diluted with deionized water. Same procedure was followed to obtain solutions containing 20, 40, 60, 80 and 100mg $L^{-1}(K^+/NH_4^+)$.

Batch adsorption

One gram (1g) of the soil sample was measured into five 50ml centrifuge tubes. The samples were equilibrated in 20ml solutions containing 20, 40, 60, 80 and 100mg L^{-1} K and 20, 40, 60, 80 and 100mg L^{-1} (K/NH_4). 2 drops of toluene was added to each sample in order to minimize microbial activities. The batch equilibration was done in a mechanical shaker for 24 hours at room temperature (25°C). Preliminary experiment has shown that, equilibrium is attained at 24 hours of agitation on mechanical shaker. At the completion of equilibration, the samples with solution were centrifuged at 4000 rpm for 30 minutes. The supernatants were thereafter filtered with Whatman filter paper No 1 and the concentration of K and NH_4 remaining in solution was determined instrumentally using flame photometer and spectrophotometer respectively.

The amount of K and NH$_4$ adsorbed was calculated from concentration difference before and after equilibration. Data obtained in the experiment were analyzed statistically using SPSS version 20.

RESULTS AND DISCUSSION

Result of particle size analysis showed that the investigated soil was clay loam in nature with 67% sand, 16 % silt and 17% clay. The calcium content of the soil (2.10 cmolkg^{-1}) was found to be lower than the critical value (5.0 cmolkg^{-1}) recommended for cocoa cultivation. The calcium content of the soil was 2.10cmolkg^{-1}. Magnesium content of the soil (0.31cmolkg^{-1}) was also below the critical level (0.8cmolkg^{-1}) required in cocoa soil. Similarly, the obtained value for extractable

K (0.26cmolkg^{-1}) was lower than the critical level (0.3cmolkg^{-1}) of potassium in soil meant for cocoa production (Egbe *et al*. 1989). Phosphorus content of the soil (11.40mgkg^{-1}) was adequate while the value obtained for organic carbon (2.25%) was lower than 3% which is the critical level for organic carbon in soil meant for cocoa cultivation (Egbe *et al*, 1989). Soil pH was 5.15 which implies that the soil is acidic in nature. Nitrogen content of the soil was 2.16%. The calculated exchangeable acidity in the soil was 2.10. On the other hand, the exchangeable Fe, Mn and Cu were 15.00, 8.52 and 0.78 mgkg^{-1} respectively. Sodium concentration was 0.52 cmol kg^{-1}. The low concentration of N, K, P, Ca and Mg in the investigated soil is an indicator pointing to the fact that the soil is deficient of plant nutrients.

Table 1: Physicochemical properties of soil.

Soil Parameter	Concentration/Amount
Particle size	
Sand	67%
Clay	17%
Silt	16%
Exchangeable bases	
K$^+$	0.26 (cmol kg^{-1})
Na$^+$	0.52 (cmol kg^{-1})
Ca^{2+}	2.10 (cmol kg^{-1})
Mg^{2+}	0.31 (cmol kg^{-1})
Exchangeable acidity	2.1
Organic carbon	2.25 %
pH (H$_2$O)1:1	5.15
Available P	11.40 mgkg^{-1}
Nitrogen	2.16 %
Exchangeable micronutrients	
Mn	8.52 (mgkg^{-1})
Fe	15.00 (mgkg^{-1})
Cu	0.78 (mgkg^{-1})
Zn	10.24 (mgkg^{-1})

Figure 1 show that 94.6% of potassium ion in solution was adsorbed in soil treated with solution containing 20 mgL^{-1}K while 30% of

solution K was adsorbed in soil treated with solution containing 20 mg L^{-1} (K$^+$/NH$_4^+$). Observation shows a 64.6% decrease in

potassium adsorption as a result of competitive adsorption between potassium and ammonium ions on the soil particles. Treatment of the soil sample with solution containing 40 mg L^{-1} K resulted in the adsorption of 63% of K in solution while only 28% of K was adsorbed in soil sample equilibrated in solution containing both ammonium and potassium ions (40 mg L^{-1} (K^+/NH_4^+). By implication, adsorption of K was reduced by 35% as a result of competitive adsorption between the two ions. In soil sample treated with 60 mg L^{-1} K, 3% of the solution K was adsorbed while 25% of solution K was adsorbed in soil sample equilibrated in solution containing both cations (60mg L^{-1} (K^+/NH_4^+). Adsorption efficiency was reduced by 18% as a consequence of both NH_4^+ and K^+ competing for same adsorption sites on the soil particles. Similar trend in K adsorption was observed when the soil sample was equilibrated in solution containing 80 and 100mg L^{-1} K General observation shows a decrease in percent adsorption as the concentration of K increased in solution. The decrease was an indication of saturation of adsorption sites with the monovalent K^+ ions. At higher solution concentration, adsorbate on adsorbent decreases due to saturation of adsorption sites as a result of increase in the number of ions competing for available binding sites (Puranik and Paknikar, 1999). Similar reduction in adsorption efficiency with increase in solution K was reported on soil obtained from North Kashmir, India (Bangroo *et al*, 2012). The observed reduction in K adsorption efficiency with increase in solution K suggests possible wastage of resources and nutrient run-off in situation where arbitrary application of K fertilizer is made without initial soil analysis. This is critical considering the fact that, soil particles have limited number of sites that could hold ions for plants' use. The significant reduction of K in soil samples equilibrated in solutions containing both K^+ and NH_4^+ was due to competitive adsorption of both ions on same

adsorption sites in soil particles. In solution containing only K^+ ions, competition for the available sites was limited to one type of competition (inter-ionic which involved only K^+ ions). However, when solution containing both K^+ and NH_4^+ ions come in contact with soil surfaces, the competition for available adsorption sites was no longer limited to K^+ inter-ionic competition. Rather, the competition for available sites becomes a multiple type (Inter-ionic competition among K^+ ions, inter-ionic competition among NH_4^+ ions and inter-ionic competition between K^+ and NH_4^+ ions). The competition between K^+ and NH_4^+ ions for same adsorption sites on the soil surface was mainly due to similarities in the chemical nature of K^+ and NH_4^+ ions. NH_4^+ and K^+ have similar valence and size properties. Consequently, they compete for the same exchangeable sites of soil particles (Bar Tal, 2011). NH_4^+ and K^+ are both monovalent cations and have similar ionic radius of 1.43 and 1.38 A^o respectively. The similarity in their chemical properties led to strong interaction between them in soil system. According to Stehouwer and Johnson, (1991) simultaneous injection of anhydrous ammonia and a KCl solution in a silty clay loam soil decreased K^+ ion fixation whereas the concentration of the exchangeable and soluble K^+ increased. The decrease in K^+ fixation was attributed to preferential NH_4^+ fixation blocking K^+ fixation and the increased exchangeable K^+ in soil solution. Certain results from field experiments indicate that, the sequence of NH_4^+ and K^+ application may influence K fixation. In a separate report, the study carried out by Chen *et al*, (2008) shows the effect of application sequence on nutrient availability. They reported that NH_4^+ at high rates of application before K fertilization to rice plant resulted in poor growth and reduced K uptake compared with NH_4^+ application after K fertilization. However, when NO_3^- was used as the N source, plant growth was not affected by the order in which N and K were

applied. The negative impact on K availability and uptake was due to the fact NH_4^+ blocked the non-exchangeable sites, thus reducing the capacity of the soil to store K to meet the need of plants. The rate of K fertilization may also influence NH_4^+ adsorption. The report of Liu *et al*, (1997) showed that in field experiments, the soil fixation capacities of both NH_4^+ and K^+ were significantly reduced by sustained high rates of K fertilization, but not by N fertilization. The influence of K application on NH_4^+ availability in soil was also reported by Kenan *et al*, (1999) where fixation of NH_4^+ was reduced by K addition before NH_4^+ was added, and that the reduction was proportional to the amount of K previously fixed. In the case of NPK 15:15:15

fertilizer in which NH_4^+ and NO_3^- are combined as nitrogen sources, the soil condition is a major factor that determines the fate of NH_4^+ in soil solution. In the field, the transformation of NH_4^+ to NO_3^- by nitrifying bacteria is usually a rapid process between days to weeks, depending on temperature, soil moisture and pH. In a situation where soil pH is low (< 5.5), soil temperature is low($< 20^oC$), nitrifying bacteria in soil are limited and organic carbon is low, the conversion of NH_4^+ to NO_3^- will be depressed or stopped (Mengel and Kirkby 1987, PNA 2017)). Consequently, there will be abundance of NH_4^+ ions to compete with K^+ ions for adsorption sites and ultimately lower the ability of the soil to store K for plant use.
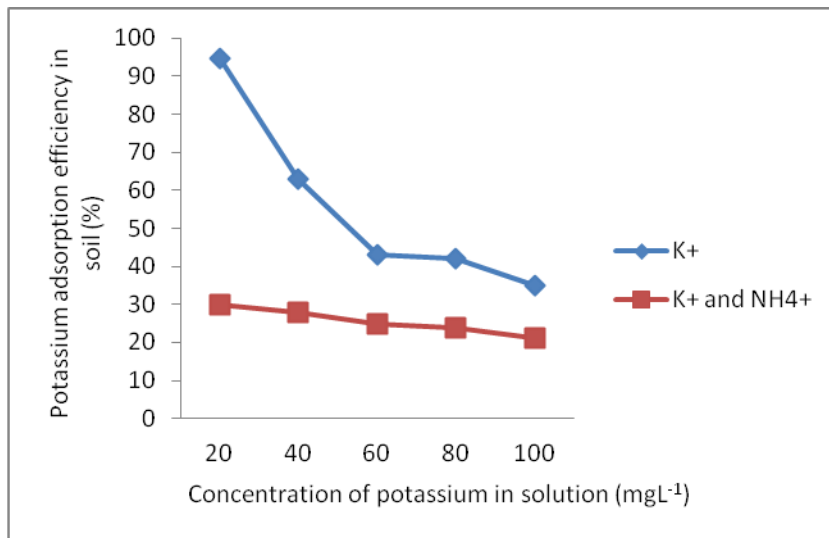

Figure 1: Potassium adsorption efficiency

Freundlich Isotherm

The Freundlich adsorption isotherm has been used to characterize adsorption of adsorbate on adsorbent. The isotherm is an empirical equation which estimates the adsorption intensity of the adsorbent towards the adsorbate.

The equation may be written as

$$q = k_f C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where q is the amount per unit mass of adsorbate (μgg^{-1}), C is the equilibrium concentration of adsorbate (μm) while k and b are contents. When Equation (1) is transformed into a logarithmic form, a straight line equation will be obtained in the form of

$$\log q = \log k_f + \frac{1}{n} \log C \ldots\ldots\ldots\ldots\ldots\ldots.. (2)$$

Where q is the quantity of adsorbed potassium and C is the equilibrium concentration. The value of k_f and n were calculated from intercept and slope of log C against log q. k_f represents adsorption capacity while n represents adsorption intensity. Results show that the calculated k_f value (11.46) obtained in soil sample equilibrated in solution containing only K^+ was significantly higher than K_f value (1.12) obtained in soil sample equilibrated in solution containing both K^+ and NH_4^+ (Table 2). The significant difference in the K_f values implies that the capacity of the soil to adsorb potassium and by extension, store potassium for plant uptake was higher in soil equilibrated in solution containing only K^+. Though soil samples in the two different solutions are of the same origin, the differences in potassium adsorption was occasioned by the competition between K^+ and NH_4^+ for adsorption site on the soil particle. Consequently, the mutual presence of both K^+ and NH_4^+ in the same solution ultimately reduced potassium adsorption capacity of the soil. In Table 2, the obtained value of n in the isotherm signifies that the intensity of potassium adsorption was higher in soil treated with solution of K^+ compared with soil sample which was treated with solution containing both K^+ and NH_4^+. By implication, the combination of K^+ and NH_4^+ in same solution reduced the intensity of potassium adsorption in the soil. In the Freundlich model, the reciprocal of the value of n is of significant importance. 1/n value = 1 indicates linear adsorption process suggesting equal adsorption energies for all sites. Linear adsorption generally occurs at very low solute concentration and low loading of the soil (Aikpokpodion et al. 2015). A value of 1/n >1 represents S type isotherm where the marginal sorption energy increases with increasing surface concentration. On the other hand a value of 1/n < 1 represents an L- type isotherm where the marginal sorption energy decreases with increasing surface concentration (Site, 2001). Considering the values obtained for 1/n in the

study, it is convenient to state that, the adsorption of potassium onto the studied soil is an L type which implies that, adsorption energy decreased with increased surface concentration.

As shown in Table 2, Freundlich equation described K adsorption with highest degree of accuracy than the rest equations. The fitness of Freundlich equation for K adsorption in soil was also reported by Bangroo et al (2012) in their study on potassium adsorption characteristics of soils under long term maize-legume cropping sequence. Similarly, potassium adsorption characteristics of four different textured alkaline calcareous soils in Pakistan was best described by Freundlich equation in a study conducted by Hannan et al. (2007)'

Langmuir Adsorption model

The Langmuir sorption equation describes reversible sorption for monolayer formation. Its linear form is expressed as

$$\frac{Ce}{X} = \frac{1}{KXmax} + \frac{C}{Xmax} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where c_e is the equilibrium concentration of potassium ($\mu g\ ml^{-1}$), x is the amount of potassium adsorbed per unit soil ($\mu g\ g^{-1}$), x_{max} is the maximum quantity of potassium adsorbed on monolayer while k is the binding energy. The slope ($\frac{1}{Xmax}$) and intercept ($\frac{1}{KXmax}$) were calculated from the plot of $\frac{Ce}{X}$ versus c. The values obtained from the Langmuir isotherm are presented in Table 2. Result shows that $47.62mgK^{-1}kg$ soil was adsorbed in soil sample equilibrated in solution containing only K^+ ions while $41.67mgK\ kg^{-1}$ soil was adsorbed in soil sample equilibrated in solution containing both K^+ and NH_4^+. It therefore implies that the adsorption of K^+ was reduced by 12.49% due to the competition for adsorption sites between K^+ and NH_4^+ in same solution. The binding energy k was lower in soil sample equilibrated in solution

containing only K^+ ions (0.014) while that of sample equilibrated in solution of K^+ and NH_4^+ was higher (0.1076). The difference in the binding energy of K^+ in the different solutions suggests that more energy is required for K^+ to bind onto the adsorption sites in soil sample treated with solution containing both K^+ and NH_4^+. This might be due to the repulsive forces between NH_4^+ and K^+ in solution thereby making the attraction of K^+ to the negatively charged surface on soil particles difficult. On the other hand, soil sample equilibrated in solution containing only K^+ had little or no counter ion which could cause repulsion in the system. The resultant effect was that the energy required by K^+ to move from the solution to the adsorption sites became minimal. The coefficient of determination value (R^2) obtained from Langmuir isotherm was 0.98 and 0.90 for solution containing K^+ and solution containing both K^+ and NH_4^+ respectively (Table 2).

Temkin adsorption model

Temkin isotherm is one of the isotherms used in describing adsorption mechanism. The equation takes into account the interaction between adsorbent and adsorbate and is based on the assumption that the free energy of sorption is a function of the surface coverage (Chen *et al.* 2008)

$$\frac{X}{m} = a_T + b_T \ln C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where x/m is the mass of potassium adsorbed per unit mass of soil (μgg^{-1}), C is equilibrium concentration of potassium in solution (μgml^{-1}) and a_T and b_T are constants. A plot of x/m against ln C gives a straight line if the adsorption process fits the model. The values of a_T and b_T were obtained from the intercept and slope respectively. The b_T value of Temkin equation is considered as the potassium buffering capacity. Potassium buffering capacity is the ability of the soil to maintain a given potassium level in soil.

Result shows that, the competition between K^+ and NH_4^+ for adsorption sites on soil particles reduced K buffering capacity of the soil from17.42 mgg^{-1} in soil treated with solution containing only K^+ ions to 12.98 in soil treated with solution of K^+ and NH_4^+.

Dubinin-Radushkevich model

Dubinin-Radushkevitch (D-R) adsorption theory is based on the postulate that the mechanism for adsorption in mocropores is that of pore filling rather than a layer-by-layer formation of a film on the walls of the pores (Hutson et al, 1998). The D-R model was used to estimate the characteristic porosity and apparent adsorption energy of the investigated soil sample. The equation can be expressed as

$$q_e = q_D \exp(-B_D[RT\ln(1+1/C_{eq}\}^2] \ldots\ldots\ldots\ldots\ldots(5)$$

Where B_D is related to the free energy of sorption per mole of potassium as it migrates to the surface of soil particles from infinite distance in the solution and q_D is D-R constant relating to the degree of potassium adsorption onto soil surface. The linear form of the equation is given as

$$\ln q_e = \ln q_D - 2B_D RT (\ln (1+1/C_e) \ldots\ldots\ldots\ldots\ldots(6)$$

D-R isotherm was obtained from a plot of ln qe against RTln(1+1/Ce) while the constants q_D and B_D were derived from the intercept and slope respectively. Results (Table 2) shows that the values obtained for q_D (37.64) in solution that contained only K^+ was higher than the value (24.73) obtained for q_D in soil sample treated with solution that contained both K^+ and NH_4^+. Result shows that, the competitive adsorption between K^+ and NH_4^+ lowered the degree of potassium adsorption in soil equilibrated in solution containing both ion types. The low coefficient of determination R^2 (Table 2) suggests that the adsorption of potassium in the studied soil did not follow the assumption of D-R model. Hence, potassium adsorption in Ikom soil was not

controlled by micropore filling. Rather, it was controlled by the principle of layer-by-layer

formation of the film on the walls of the pores in soil.

Table 2: Constants obtained from various adsorption equations

	Freundlich			Langmuir			Temkin			D-R		
	K_f (mgg^{-1})	n	R^2	K (Lmg^{-1})	X_{max} (mgg^{-1})	R^2	b_T	a_T (mgg^{-1})	R^2	q_D (mgg^{-1})	B_D (mol^2/KJ^2)	R^2
K^+	11.46	3.63	0.99	0.0104	47.62	0.98	17.42	8.85	0.79	37.64	0.006	0.84
K^+/NH_4^+	1.12	1.36	0.99	0.1076	41.67	0.90	12.98	3.60	0.99	24.73	0.016	0.98

CONCLUSION

The study shows the significance of chemical interaction between potassium and ammonium ions in soil as it affects the bioavailability of potassium for plants' use. The storage capacity of the soil for potassium as plant nutrient was reduced due to competition between NH_4^+ and K^+ for adsorption sites. For optimal utilization of fertilizer by cacao plant, possible chemical interactions and chemical properties of nutrient elements or compounds intended for use in formulating compound fertilizer has to be considered before they are combined should the soil condition becomes unfavorable for NH_4^+ oxidation to NO_3^- Hence, unfavorable chemical interactions among fertilizer components could adversely affect the bioavailability of the nutrients in fertilizer.

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