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Studies on adsorption mechanism and kinetics of magnesium in selected cocoa growing soils in Nigeria

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ABSTRACT

Several soil evaluations have found magnesium deficient in most cocoa plantations in Nigeria. Authors have recommended the use of magnesium fertilizers to address the deficiency. For appropriate fertilizer application and effective utilization of applied fertilizer, understanding the adsorption kinetics and magnesium holding capacity of each soil will help in making precise recommendation in order to prevent wasting of resources and contamination of the environment with un-adsorbed magnesium. Soil samples were collected with soil auger at a depth of 0-30cm from selected cocoa plantations in Lodu, Itu, Ikom, Asaba and Uhonmora in Abia, Akwa Ibom, Cross River, Delta and Edo States respectively. One gram (1.0 g) of each sample was equilibrated with 30ml of 20, 40, 60, 80 and 100 mg Mg L^{-1} solution. Another portion (1.0 g) of each sample was equilibrated with 30ml of 70 mg Mg L^{-1} for 40, 80, 120 and 140 minutes to study the kinetics of Mg^{2+} ions in soil. The data generated were fitted into various adsorption Isotherms and kinetic models. Results showed that, Freundlich model best described the adsorption of magnesium indicating Mg adsorption on heterogeneous surfaces. Mass transfer kinetic model best described the kinetics of Mg^{2+} adsorption. Sample obtained from Cross River State had the highest adsorption capacity for magnesium compared with the rest of the soils. Clay and organic carbon were the main soil properties that influenced Mg^{2+} adsorption in the soils.

Keywords: Cocoa, adsorption, magnesium, Isotherm, kinetics

INTRODUCTION

Cocoa has contributed immensely to the economy and gross domestic product (GDP) of the Nation Nigeria [1]. The discovery of petroleum as a commodity of commerce has negatively affected the commitment of the government to the production of cocoa which used to be the nation's main source of foreign earnings [2]. The low yield of cocoa has been partly attributed to nutrients depletion without replacement in most cocoa plantations in Nigeria [3]. The study carried out by Ogunlade *et al* [4] revealed that, most Nigerian cocoa farmers do not apply fertilizers on their farms and the nutrient replacement through leaf litter fall is not sufficient to make up for the lost nutrients during fruiting and seed development. The type of clay mineral present in most Nigerian cocoa soils demands continuous fertilization of the soils. This might be the reason why Lombi and Fayemi in 1975 predicted deficiency of magnesium in Nigeria soils [5].

Ipinmoroti *et al*. reported deficiency of magnesium in some cocoa plantations in Ibadan Southwestern Nigeria. Aikpokpodion also reported deficiency of magnesium in selected cocoa plantations in Ondo State, Nigeria.

Magnesium (Mg) deficiency is a detrimental plant disorder that occurs most often in strongly acidic, light, sandy soils, where magnesium can be easily leached away. Magnesium is an essential macronutrient found from 0.2-0.4% dry matter and is necessary for normal plant growth [6].

Magnesium has an important role in photosynthesis because it forms the central atom of chlorophyll. Therefore, without sufficient amounts of magnesium, plants begin to degrade the chlorophyll in the old leaves. This causes the main symptom of magnesium deficiency, chlorosis, or yellowing between leaf veins, which stay green, giving the leaves a marbled appearance. Due to magnesium's mobile nature, the plant will first break down chlorophyll in older leaves and transport the Mg to younger leaves which have greater photosynthetic needs. Therefore, the first sign of magnesium deficiency is the chlorosis of old leaves which progresses to the young leaves as the deficiency continues [7]. Magnesium also is a necessary activator for many critical enzymes, including ribulosbiphosphate carboxylase (RuBisCO) and phosphoenolpyruvate carboxylase (PEPC), both essential enzymes in carbon fixation. Thus low amounts of Mg lead to a decrease in photosynthetic and enzymatic activity within the plants. Magnesium is also crucial in stabilizing ribosome structures, hence, a lack of magnesium causes depolymerization of ribosomes leading to pre-mature aging of the plant [8]. After prolonged magnesium deficiency, necrosis and dropping of older leaves occurs. Plants deficient in magnesium also produce smaller, woodier fruits. Based on the importance of magnesium in plant nutrition, application of magnesium fertilizer to magnesium deficient cocoa soils was recommended by Ipinmoroti *et al*., Ogunlade et al., and Aikpokpodion.

The objective of this research is to investigate the adsorption mechanisms and kinetics of magnesium in selected soils within Nigeria on which cocoa is grown. Sorption kinetics is investigated to develop an understanding of controlling reaction mechanisms (e.g. surface versus intra-particle diffusion) of sorption reactions. Kinetic data can be used to predict the rate at which the target adsorbate is removed from soil solution and equilibrium adsorption isotherms are used to quantify the adsorptive capacity of the soil.

EXPERIMENTAL SECTION

Sample collection
Soil samples were collected at a depth of 0-15cm with soil auger from selected cocoa plantations at Ikom (Cross River State), Itu (Akwa Ibom State), Uhonmora (Edo State), Lodu (Abia State) and Delta State. The soil samples were air-dried and sieved with 2 mm sieve.

Sorption:
One gram of each of the samples was introduced into 30 ml capacity sample bottles and 15 ml of 20, 40, 60, 80 and 100 mg magnesium per liter was added to each sample. The soil samples were shaken on a mechanical shaker for 16 hours equilibration at 25^{o}C. After completion, the equilibrated samples were centrifuged and filtered with Whatman filter Paper No 1. The concentration of magnesium in the filtrate was determined with Buck Scientific Atomic Absorption Spectrophotometer. The data generated were fitted into Freundlich, Temkin and flory-Huggins equations to determine the various constants in each of the models.

Sorption kinetics:
The kinetics study was carried out by adding 30 ml of 70mg Mg L^{-1} solution into sample bottles containing 1 gram of each of the studied soils. The bottles and contents were equilibrated for 40, 80, 120 and 140 minutes in order to study the adsorption mechanism in relation to contact time. At the end of each equilibration time, the samples bottles were transferred to the centrifuge and the samples centrifuged for 5 minutes at 3000 rpm followed by filtration with Whatman filter paper. Each filtrate was analyzed for equilibrium concentration of magnesium left in the solution after sorption process using Buck Scientific Atomic Absorption Spectrophotometer. The data obtained were fitted into Pseudo-first order, Pseudo-second order, Intra-particle diffusion, Mass transfer and Elovich equations.

Physicochemical analysis of soil samples:
The samples were leached with 1N ammonium acetate. The leachate was analyzed for exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) determination [9]. Soils were analyzed for particle size by the Boyocous hydrometer method soil pH was measured with glass electrodes in 1:2.5 soil-water suspensions. The organic carbon was determined after

using the method of Walkey and Black, [10]. Available Phosphorus was determined using Bray and Kurtz method [11].

RESULTS AND DISCUSSION

Freundlich Adsorption Isotherm:

The Freundlich isotherm is an empirical equation which estimates the adsorption intensity of the adsorbent towards the adsorbate. Freundlich equation is suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau indicates a multilayer adsorption [12]. The model is represented by the equation

$q = K_f\, C_e\, q^{1/n}$ [13].

The linearized form of the adsorption isotherm was used to evaluate the sorption data and is represented as

$\ln q = \ln K_f + 1/n \ln C_e$,

where C_e is the equilibrium concentration (mg L^{-1}), q is the amount adsorbed (mg g^{-1}) , K_f and n are constants incorporating parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The values of K_f and n were calculated from the intercept and slope of the Freundlich plots respectively. According to [14], *n* value between 1 and 10 represents beneficial adsorption. In the studied soils, the values of n ranged between 1.43 and 3.09 (Table 2). Result implies that, beneficial adsorption of Mg on heterogeneous sites took place in the course of adsorption. Kuo and Lotse [15] reported that, exponent of the Freundlich equation (1/n) was independent of time and temperature but dependent of soil properties.

From the report of Juang et al., magnitude of K_f shows easy separation of Mg from solution while n shows adsorption capacity. It therefore suggests that, under the same fertilizer application condition, soil obtained from Abia State will have more magnesium ions separated from soil solution than the rest of the soils considered in the study. This is however, attributable to the physicochemical properties of Abia soil.

The high coefficient of determination R^2 in Freundlich isotherm compared with other Isotherms considered in the study is an indication that, the adsorption of Mg was on the heterogeneous sites with varying energies of adsorption. [16] reported that, the adsorption of heavy metal in soils was on heterogeneous adsorption sites. [17] reported that, the adsorption of Zn in Pakistan soils followed a Freundlich adsorption isotherm. Our findings show that K_f and n which are Freundlich constants relating to affinity of Mg ions for the soil solid phase and adsorption intensity respectively had positive correlation with organic carbon and CEC in the studied soils (Table 4). This suggests that, the intensity and rate of adsorption increased with CEC, and organic carbon of the soils. Table 1 show that, soil sample obtained from Abia State had the highest values of CEC. Hosseinpur and Dandanmozd [18] reported that, distribution coefficient (K_f) significantly correlated with CEC. Reyhamitabar *et al*., [19] in their study on Zn retention in twenty calcareous soils of central Iran, reported a significant relationship between Freundlich K_f and CEC. Karimian and Moafpourian [20] reported that, in calcareous soils of the Southwestern part of Iran, Freundlich Kf showed positive correlation with CEC and organic matter. Elrashidi and O'Connor [21] reported a significant relationship between Freundlich coefficients and CEC and pH but not organic matter of the soil. Amjad *et al*., [22] reported significant positive correlation between Freundlich K_f and percent clay, organic matter, $CaCO_3$ and pH.

Flory-Huggins Isotherm:

The Flory-Huggins model was used in order to account for the degree of surface coverage characteristics of magnesium on the studied soils. The Flory-Huggins model is represented by equation

$\log \frac{\theta}{C_o} = \log K_{FH} + n_{FH} \log (1- \theta)$

Where

$\theta = (1 - \frac{C_e}{C_o})$

θ is the degree of surface coverage characteristics of magnesium on the studied soils, n_{FH} is the number of Mg^{2+} ions occupying sorption sites, K_{FH} is the equilibrium constant of adsorption and C is the equilibrium Mg^{2+} ion concentration.

A plot of log ($\frac{\theta}{C_o}$) versus log (1- θ) yielding a straight line confirms the application of the model to magnesium adsorption.

The equilibrium constant K_{FH} obtained from the Flory-Huggins isotherm can be used to compute the apparent Gibb's free energy of sorption; ΔG^o is the fundamental criterion of spontaneity. Reaction occurs spontaneously at a given temperature if ΔG^o is a negative quantity. ΔG^o (KJ^{-1}) was evaluated using the following equation

$$\Delta G^o = -RT \ln (K_{FH})$$

Where

R is the universal gas constant, 8.314J/molK^{-1} and T is absolute temperature.

The isotherm data (Table 2) showed that, the apparent number 'n_{FH}' of Mg^{2+} ions occupying adsorption sites was highest in soil obtained from Cross River while it was lowest in soil obtained from Abia. The higher rate of occupancy of the adsorption sites by Mg^{2+} ions in Cross River soil compared to the rest of examined soils was enhanced by the physicochemical properties of the soil. Among the five soils investigated, soil obtained from Cross River had the highest percentage of clay, organic matter and manganese. These physicochemical properties by nature contribute to sorption of cations on soil surfaces. Soil clay has negatively charged edges which attract cations to its surfaces by electrostatic force of attraction. The carbonyl group, amine group and sulpho group present in soil organic matter are all negatively charged and by sorption principle, have the capacity to form bond with positively charged cations in soil solution. The hydrous oxides associated with manganese in soil could also bind with cations in solution. All these soil properties were higher in soil obtained from Cross River State compared with the rest.

The correlation of Flory-Huggins constants with soil physicochemical properties (Table 3) confirms contributions of clay, Mn and organic matter to the rate of magnesium at which magnesium occupies the adsorption sites on the soil surfaces. Manganese, clay and organic matter had positive correlations with K_{FH} and n_{FH} at significant levels (Table 3). The relatively high correlation coefficient (R^2) which ranged from 0.63 to 0.98 is an indication that, Flory-Huggins model did not give an excellent fit for the description of Mg^{2+} onto the studied soils.

Temkin Isotherm:

The Temkin model assumes that, the adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interactions. Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes account of the interaction between adsorbents and cations to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [23]

$$qe = \frac{RT}{bT} \ln (K_T.C_e)$$

The linear form of Temkin equation is

$$qe = \frac{RT}{bT} \ln K_T + \frac{RT}{bT} \ln C_e$$

Where

b_T is the Temkin constant related to heat of sorption (J/mg) and K_T is the binding constant corresponding to the maximum binding energy (L/g).

The Temkin constants b_T and K_T are calculated from the slope and intercept of the plot of qe versus ln C_e respectively.

The values of the b_T and K_T obtained in the studied soils are given in Table 2. The values of b_T ranged from 61.82 to 138 while K_T ranged between 1.28 and 14.58. Result showed that, soil obtained from Cross River had the highest equilibrium binding constant corresponding to the maximum binding energy (K_T) while soil from Akwa Ibom had the least binding energy. This suggests that, desorption of adsorbed Mg^{2+} ions from the adsorption sites of the studied soils will be lowest in Cross River soil and highest in Akwa Ibom soil. From plant nutrition point of view, the release (desorption) of adsorbed Mg^{2+} ions into soil solution for plant uptake will be faster in Akwa Ibom soil and slowest in soil sample obtained from Cross River. Magnesium retaining capacity in Cross River soil is beneficial in terms of nutrient reservation for plant uptake. On the other hand, the leaching of adsorbed magnesium may be higher in Akwa Ibom soil compared with the rest due to the low maximum binding energy between Mg^{2+}

and soil surface. The high maximum binding energy between Mg^{2+} ions and the soil surfaces obtained in Cross River soil compared with the rest of the examined soils is due to its physicochemical properties. Table 1 shows that, soil sample obtained from Cross River had the highest percentage of clay, organic matter and manganese. This was confirmed by the linear correlation between soil physicochemical properties and Temkin constants. Result (Table3) showed that, the maximum binding energy (K_T) had positive correlation with soil manganese, copper, organic matter and clay at significant level while it was negatively correlated with percent sand content at significant level.

Pseudo First-order kinetics:
The adsorption kinetic data were described by the Lagergreen Pseudo first-order model [24] which is the earliest known equation describing the adsorption rate based on the adsorption capacity. It is assumed that one magnesium, ion is sorbed onto one adsorption site on the soil surface

$$A + Mg^{2+}_{aq} \xrightarrow{k1} AMg_{solid\ surface}$$

Where A represents unoccupied sorption site on the soil surface and k_1 is the pseudo first order rate constant (h^{-1})

The differential equation is generally expressed as

$$\frac{dqt}{dt} = K_1(q_e - q_t)$$

Where qe and qt are the adsorption capacities at equilibrium and at time t, respectively (mg/g), K_1 is the rate constant of Pseudo first order adsorption (L/min). Integrating equation above for the boundary conditions t = 0 to t and qt = 0 to qt gives

Where qe and qt (mg g^{-1}) are the adsorption capacities at equilibrium and at time t (h), respectively.

In order to obtain the rate constants, the values of log (qe- qt) were linearly correlated with *t* from which K_1 and predicted qe were determined from the slope and intercept of the plot respectively.

$$\text{Log}\ (q_e - q_t) = \log\ (q_e) = \frac{K1}{2.303}\ t$$

According to the assumption of the Pseudo-first order kinetics, the variation in the rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and the rate of adsorption will not be linear when pore diffusion limits the adsorption process [25]. Table 4 shows that, the predicted qe calculated from the plot ranged from 44.56 to 66.85. The coefficient of determination (R^2) ranged from 0.87 to 0.99. The correlation coefficients obtained with first order equation were relatively lower than the data obtain with second order equation for most of the studied soils except in soil obtained from Akwa Ibom. This implies that, the adsorption of Mg^{2+} ions onto the soils was not controlled by first order reaction. Hence, the initial solution concentration of magnesium was not a limiting rate in the adsorption of magnesium onto the studies soils.

Pseudo Second-Order Kinetics:
The pseudo second order rate expression, has been applied for analyzing chemisorptions kinetics from liquid solutions [26, 27]

The adsorption kinetics of Mg^{2+} ions onto soil surfaces may be described by the Pseudo second order model. The differential equation is generally given as

$$\frac{dqt}{dt} = K_2\ (qe - qt)^2$$

Where K_2 is the second-order rate constant of adsorption. Integrating equation above for the boundary conditions q_t = 0 to q_t at t = 0 to t and rearranging gives the following linear form

$$\frac{t}{qt} = \frac{1}{K_2 q^2 e} = \frac{1}{q_e}\ t$$

Where K_2 is the rate constant for pseudo-second order adsorption (g mg^{-1} h^{-1}) and $K_2 q_e^2$ or h (mg g^{-1} h^{-1}) is the initial adsorption rate.

This model assumes that one magnesium ion is sorbed onto two sorption sites on the soil surface. If pseudo-second order is applicable, the plot of $1/q_t$ versus t should give a linear relationship from which qe and K can be determined from the slope and intercept of the plot respectively. Where *t* is the contact time (min) q_e is the predicted adsorbed Mg^{2+} (mg/g) and qt (mg/g) is the amount of Mg adsorbed at equilibrium at any time *t*. Result (Table 4) shows that, pseudo second order constant K ranged from 21.83 to 36.10. Soil obtained from Abia had the highest K value. The coefficient of determination R^2 ranged from 0.93 to 0.99. The R^2 values obtained with pseudo second order kinetics in the studied soils are much higher than the coefficient of determination obtained with first-order kinetics. This suggests that, second order kinetics gave better fits in describing Mg ion sorption in the studied soils than the first-order kinetics. This is an indication that, Mg^{2+} ions were adsorbed onto the soil surface via chemical interaction. This is in line with the findings of [28]. By way of further explanation, the adsorption of Mg^{2+} onto the soil surfaces is proportional to the square of the number of unoccupied sites [29] meaning that, the sorption of Mg^{2+} ions in the studied soils involves two species which include magnesium in soil solution and the soil surfaces.

The Mass Transfer model:
The mass transfer kinetic model was used to describe the adsorption mechanism of Mg^{2+} onto the studied soils. According to Qadear and Akhtar, [30]

$$C_o – C_t = D \exp (K_o t)$$

Where
C_o is the initial magnesium ion concentration at time *t*, *t* is the equilibrium time (min), D is the fitting parameter, K_o is a constant relating to the mass transfer adsorption coefficient. A linearized form of the equation is

$$\ln (C_o-C_t) = \ln D + K_o t$$

A plot of ln (C_o-C_t) versus *t* gave a linear relationship where ln D and K_o were determined from the intercept and slope respectively.

Result (Table) shows that, D which is the fitting parameter ranged from 68.65 to 80.88 in which soil sample obtained from Akwa Ibom had the highest D value. The correlation coefficient (R^2) ranged between 0.98 and 0.99 which suggests that, the sorption of Mg^{2+} ion onto the soil surfaces was controlled by mass transfer. Mass transfer is the movement of a chemical species in a fluid mixture caused by some forms of driving force. There are two main mechanisms of mass transfer: diffusion and mass transport by convection. However, the rate of diffusion of ions between soil solution and soil surfaces is generally low due to molecular collisions that give rise to extremely strong hindrance to the movement of molecules [31].

Elovich Kinetic model:
The adsorption kinetics of Mg^{2+} onto the studied soils was evaluated using the Elovich equation. According to Chen and Clayton [32], the equation is expressed as

$$\frac{dqt}{dt} = \alpha \exp (-\beta\ qt)$$

Where
Qt is the sorption capacity at time t (mg g^{-1}), α is the initial adsorption rate (mg $g^{-1}min^{-1}$), β is the desorption constant (gmg^{-1}) during any one experiment. For the purpose of simplification of Elovich equation, Chen and Clayton assumed α β t >>1 and by applying the boundary conditions qt = 0 at t = 0 and qt at t = t, the equation becomes

$$qt = \frac{1}{\beta} \ln (\alpha\ \beta) + \frac{1}{\beta} = \ln t$$

A plot of qt versus ln t gave a linear relationship with slope ($\frac{1}{\beta}$) and intercept ($\frac{1}{\beta}$) ln (α β).

Result (Table 5) shows that, β ranged from 0.12 to 0.39 while ($\frac{1}{\beta}$) ln (α β) ranged from 0.90 and 23.94. According to Chen and Clayton, a decrease in α indicates reduction in adsorption of the adsorbate. Result showed that, the rate of adsorption was highest in soil obtained from Edo and lowest in Delta soil. However, due to the low correlation coefficient (R^2) obtained by fitting data into the equation , Elovich equation did not give good fit for describing Mg^{2+} adsorption.

Intra-particle diffusion model:
The Intra-particle model, according to [33] and [34] is expressed as
$R = K_{id} (t)a$

A linearized form of the equation is
$\log q_t = \log K_{id} + 0.5 \log t$
Where
q_t is the amount of Mg^{2+} ions adsorbed at time t (mg g^{-1}), t is the contact time (min)

The model is based on the assumption that, diffusion into the interior pores of the soil particles from the soil solution controls the adsorption of Mg^{2+} ion onto the studied soils.

An understanding of adsorption mechanisms facilitates the determination of the rate-limiting step. The overall rate of adsorption can be described by the following three steps: (1) film or surface diffusion, where the sorbate is transported from the bulk solution to the external surface of sorbent, (2) intra-particle or pore diffusion, where sorbate molecules move into the interior sites of the sorbent particles, and (3) adsorption on the interior sites of the sorbent [35]. Since the adsorption step is very rapid, it is assumed that it does not influence the overall kinetics. The overall rate of adsorption process, therefore, will be controlled by either surface diffusion or intra-particle diffusion. The Weber-Moris intra-particle diffusion model has often been used to determine if intra-particle diffusion is the rate-limiting step [36, 37, 38]. According to this model, a plot of qt versus $t^{1/2}$ should be linear if intra-particle diffusion is involved in the sorption process and if the plot passes through the origin then, intra-particle diffusion is the sole rate-limiting step [39]. Result (Table 5) shows that, the intra-particle diffusion rate constant K_{id} ranged from 14.97 to 42.23. This suggest that, intra-particle diffusion of Mg^{2+} ions from the soil solution onto the soil surfaces was highest in soil obtained from Edo and lowest in soil from Akwa Ibom. The relatively high percentage of sand in Edo soil may be responsible for higher diffusion of the sorbate. The plot of the graph obtained in the study did not pass through the origin which suggests that, intra-particle diffusion was not the sole rate - limiting step. It has also been suggested that in instances when q_t versus $t^{1/2}$ gives multi-linear plots, it means two or more steps govern the adsorption process[40, 41]. Result (Figure 8) indicated multi-linear three steps in the plot of q_t versus $t^{1/2}$ for all the studied soils. This is an indication that, three steps were involved in the sorption of Mg^{2+} onto the soil surfaces.

Table 1: Physicochemical properties of the studied soils

	Cross River	Abia	Edo	Akwa Ibom	Delta
Ca (cmol/kg)	2.1	1.5	0.85	1.26	0.97
Mg (Cmol/kg)	0.31	0.36	0.06	0.18	0.09
Na (Cmol/kg)	0.52	0.78	0.46	0.92	0.45
K(Cmol/kg)	0.26	1.10	0.05	0.08	0.07
Al(mg/kg)	0.48	0.54	0.37	0.36	0.38
Fe (mg/kg)	2.4	6.00	4.80	2.40	4.90
Mn (mg/kg)	8.52	2.52	1.26	0.90	1.16
Cu (mg/kg)	0.78	0.36	0.18	0.36	0.24
Organic Carbon(%)	3.18	2.34	1.07	1.10	1.06
Sand (%)	23.80	60.20	82.20	79.80	61.20
CEC	3.19	3.74	1.42	2.44	1.58
Silt (%)	18.30	10.30	4.60	5.30	11.25
Clay (%)	57.90	29.50	13.20	14.90	27.55

Table 2: Values of Isotherm constants obtained from the sorption experiment

	Temkin			Freundlich			Flory- Huggins			
Location	b_T	K_T	R^2	Kf	n	R^2	K_{FH}	n_{FH}	R^2	ΔG
Cross River	81.39	14.58	0.76	6.36	1.80	0.99	1.72	16	0.71	-1230
Abia	61.82	4.52	0.79	7.60	3.09	0.99	1.67	6.97	0.98	-1165
Edo	68.50	3.49	0.86	6.67	2.57	0.99	1.59	9.66	0.89	-1054
Akwa Ibom	138.33	1.28	0.54	3.06	1.43	0.98	1.55	10.45	0.79	-996
Delta	113.86	1.51	0.65	3.68	1.55	0.99	1.58	14.03	0.63	-1039
Mean	92.78	5.08	0.72	5.47	2.09	0.99	1.62	11.42	0.8	-1097
Stdev	32.39	5.48	0.13	1.98	0.71	0.02	0.07	3.59	0.14	97.11

The first sharper portion was the external surface or film diffusion, the second was a gradual/linear adsorption where intra-particle or pore diffusion was rate limiting and the third portion was the final equilibrium stage where intra-particle diffusion starts to slow down due to extremely low adsorbate concentration in the solution. As the plot did not pass through the origin, intra-particle diffusion was not the only rate-limiting step rather, there were three processes controlling the adsorption rate but only one was rate limiting in any particular time range. According to [42], the deviation from origin may be due to variation of mass transfer in the initial and final stages of adsorption while [43] stated that, the deviation of the plot from origin was indicative of pore diffusion being the only controlling step and not the film diffusion. Mohamed et al. [44] reported that, the adsorption of chromium (VI) onto cement kilm dust had three steps of adsorption in the plot of q_t versus $t^{1/2}$. Hardiljeet et al., also reported three steps for the adsorption of cadmium ions onto nanozerovalent iron particles. The intercept of the plot provides an estimation of the thickness of the boundary layer [45]. The larger the intercept, the greater the contribution of surface sorption in the rate-controlling step [46]. Result (Table 5) showed that, soil sample obtained from Edo had the least value of intercept 'a' in the intra-particle diffusion model which indicates the lowest thickness of the boundary layer. This might be connected to the low clay content of the soil compared to the rest of the soil samples.

Table 3: Correlation between Isotherms constants and soil properties

	Temkin		Flory-Huggins		Freundlich	
	b_T	K_T	K_{FH}	n_{FH}	Kf	n
Ca	-0.204	0.873	0.848	0.846	0.326	-0.03
Mg	-0.353	0.563	0.78	0.438	0.491	0.354
Na	0.369	-0.287	-0.19	-0.299	-0.213	0.010
K	-0.57	0.117	0.544	-0.096	0.648	0.750
Al	-0.653	0.537	0.858	0.350	0.733	0.613
Fe	-0.557	-0.419	-0.12	-0.596	0.469	0.738
Mn	-0.336	0.992**	0.880*	0.974**	0.397	-0.058
Cu	-0.097	0.914*	0.781	0.936*	0.200	-0.213
C	0.496	0.904*	0.973**	0.806	0.587	0.235
CEC	-0.324	0.498	0.725	0.370	0.471	0.369
Sand	0.262	-0.894*	-0.865	-0.900	-0.296	0.115
Silt	-0.224	0.831	0.824	0.850	0.243	-0.144
Clay	-0.273	0.910*	0.875	0.913*	3.12	-0.105

*Key: *= significant at P < 0.05*
*** = Significant at P < 0.01*

Table 4: Constants of Pseudo-first order, Pseudo-second order kinetics and Intra-particle diffusion models

Pseudo	First order kinetic			Mass transfer kinetics			Pseudo second order kinetics		
Location	q_e	K_1	R^2	D	K_o	R^2	K	qe	R^2
Cross River	1.20	58.56	0.93	75.19	-0.001	0.99	26.53	0.0013	0.98
Abia	1.15	56.05	0.92	71.95	-0.001	0.99	28.57	0.0017	0.96
Edo	1.10	44.56	0.87	68.65	-0.001	0.99	31.45	0.0025	0.90
Akwa Ibom	1.26	66.85	0.99	80.88	-0.001	0.99	21.83	0.083	0.99
Delta	1.26	55.56	0.93	75.11	-0.001	0.98	27.03	0.011	0.97
Mean	1.194	56.32	0.93	74.35	-0.001	0.99	27.08	0.019	0.96
Stdev	0.069	7.982	0.05	4.53	0	0.01	3.506	0.035	0.035

Table 5: Constants of Elovich and Intra-particle diffusion models

	Elovich Equation			Intra-particle diffusion		
	β	$1/\beta \ln(\alpha\beta)$	R^2	a	K_{id}	R^2
Akwa Ibom	0.12	6.00	0.96	0.27	14.97	0.98
Edo	0.39	23.95	0.63	0.07	42.23	0.72
Abia	0.22	12.74	0.93	0.13	31.00	0.93
Cross River	0.17	6.63	0.98	0.18	24.88	0.99
Delta	0.13	0.90	0.97	0.23	20.98	0.99
Mean	0.21	10.04	0.89	0.176	26.812	0.922
Stdev	0.11	8.84	0.15	0.079	10.407	0.115

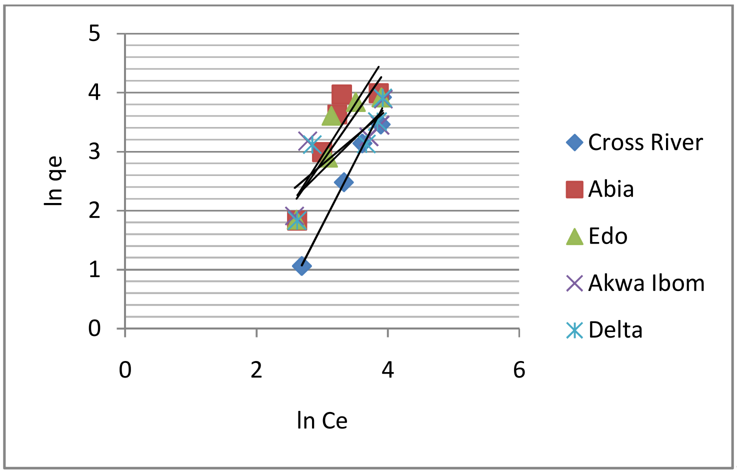

Figure 1: Freundlich Isotherm

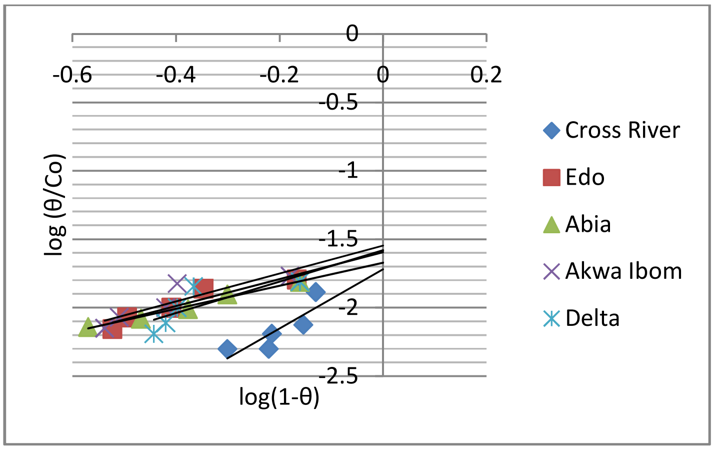

Figure 2: Flory-Huggins Isotherm

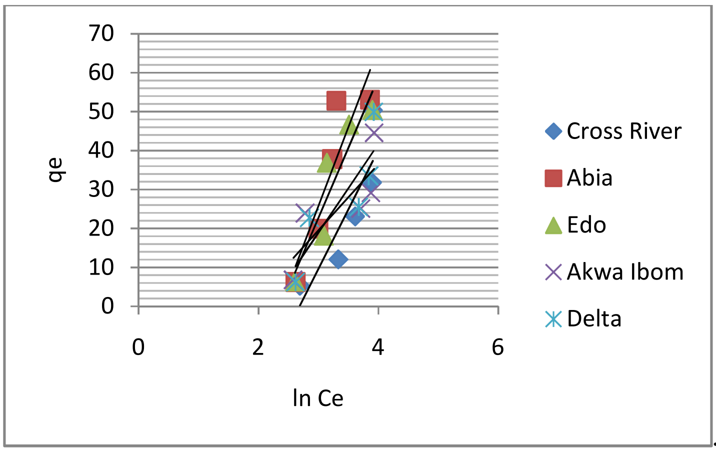

Figure 3: Temkin Isotherm

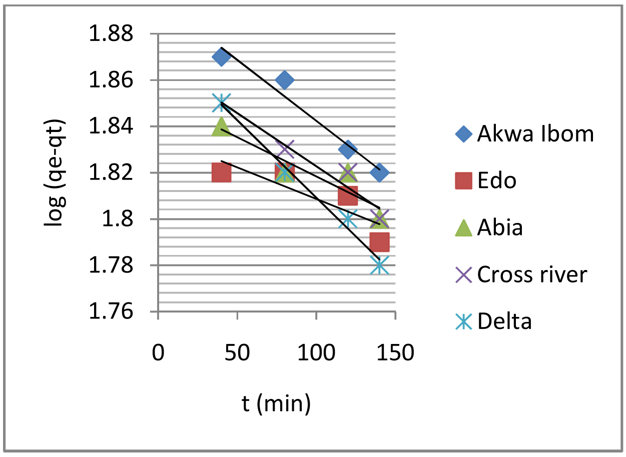

Figure 4: Pseudo-first order kinetics

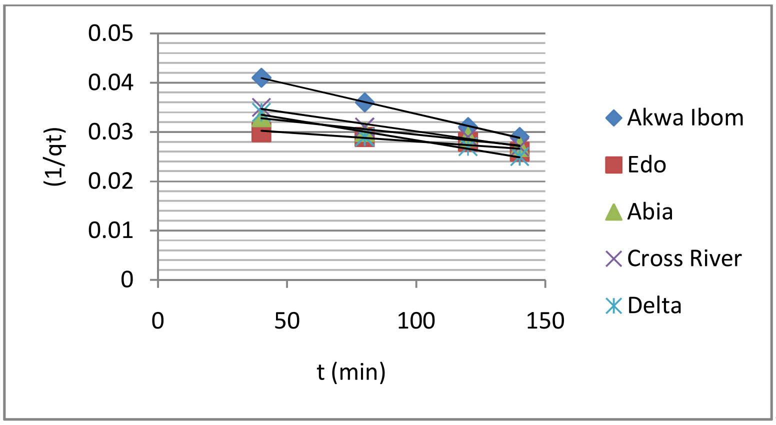

Figure 5: Pseudo-second order kinetics

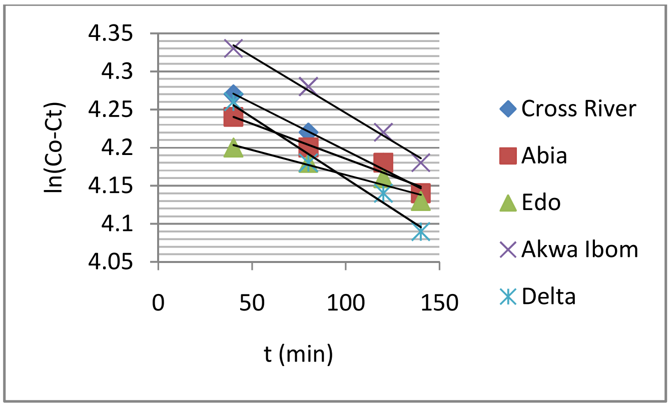

Figure 6: Mass transfer kinetics

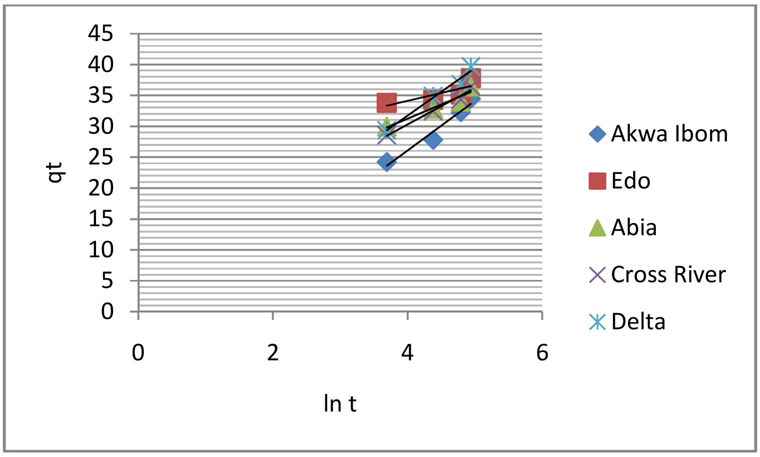

Figure 7: Elovich Model kinetics

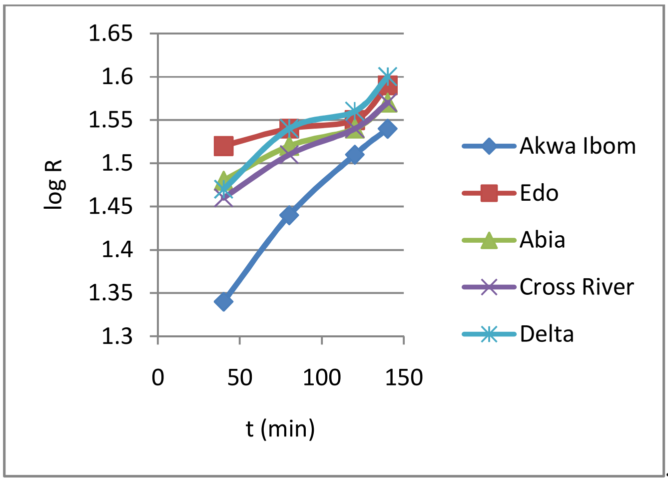

Figure 8: Intra-particle diffusion model

CONCLUSION

The study showed that, magnesium was favorably adsorbed by all the studied soils. Soils obtained from Ikom in Cross River State had the highest adsorption capacity for magnesium adsorption among all the studied soils. Freundlich model best described Mg^{2+} adsorption while the rate of adsorption was mainly controlled by mass transfer and intra-particle diffusion of Mg^{2+} from soil solution to adsorption sites. Clay and organic matter were the main soil properties that influenced the adsorption of magnesium.

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