



Magnesium Adsorption in Selected Cocoa Growing Soils Within Southwestern Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author PEA designed the study and wrote the the manuscript. Authors KNA and TO managed the literature searches while author SMO handled the Chemical analyses of the samples. All authors read and approved the final manuscript.

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ABSTRACT

Magnesium is one of the vital nutrients required by *Theobroma cacao L.* for optimum growth and yield. Several authors have reported the deficiency of magnesium in Nigerian cocoa plantations and ended up recommending the application of magnesium fertilizer based on agronomic soil test. Application of fertilizer without considering the potential of each soil to retain certain proportion of the applied fertilizer will lead to reduced available Mg in the soil solution. The study was carried out to evaluate the sorption capacity of selected cocoa growing soils in southwestern Nigeria. Soil samples were equilibrated with 20, 40, 60, 80 and 100 mg Mg L⁻¹. Result showed that, Freundlich equation best described the adsorption of magnesium onto the soil surfaces. Adsorption of magnesium was highest in Owena soil. Hence, more magnesium fertilizer will be required by Owena soil compared with Ekiti, Ibadan, Ile-Ife and Bodo soils to produce equal amount of available magnesium ions in soil the solution.

Keywords: Isotherm; adsorption; Nigeria; fertilizer; Freundlich; Langmuir.

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1. INTRODUCTION

Low yield of cocoa has been partly attributed to nutrients depletion without replacement in most cocoa plantations in Nigeria [1]. The findings of [2] 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 (1:1 kaolinite) requires continuous fertilization of the soils for optimal yield. That was why [3] predicted deficiency of magnesium in Nigeria soils. Ipinmoroti et al. [1] reported deficiency of magnesium in some cocoa soils in Ibadan Southwestern Nigeria, [4] also reported deficiency of exchangeable magnesium in selected cocoa plantations in Ondo State, Nigeria.

Magnesium being the only cation in chlorophyll is at the core centre of the molecule and it is an essential ingredient for healthy plants [5]. Reduction in soil exchangeable magnesium could cause nutritional imbalance in plants [6].

In principle, there are two reasons for Mg deficiency to occur: Absolute deficiency and cation competition. Absolute deficiency can be a consequence of (1) Low Mg contents in the source rocks, (2) Mg losses from the soil e.g. by mobilization and subsequent leaching and (3) Of long-term unbalanced crop fertilization practice neglecting Mg depletion of soils through crop Mg removal. Cation competition is a consequence of nutrient imbalances in soils. It is commonly known that the uptake of Mg is strongly influenced by the availability of other cations like NH_4^+ , Ca^{2+} and K^+ [7].

In contrast to other cations like K^+ , Ca^{2+} and NH_4^+ Mg is comparatively mobile in soils. The behavior of Mg in soils can be ascribed to its unique chemical property. Whereas the ionic radius of Mg is smaller than that of Ca^{2+} , K^+ or Na^+ , its hydrated radius is substantially larger [8,9]. Consequently, magnesium is less bound to soil surfaces leading to higher Mg concentrations in the soil solution compared to other cations. This however, does not remove the possibility of magnesium fixation in soil due to cationic interaction with reactive surfaces within the soil system [10]. Knowing the vital role of magnesium in plant nutrition, several scientists have recommended its application in cocoa plantations where the nutrient was found limiting.

Generally, the availability of applied fertilizer in soil solution is controlled by adsorption - desorption process and its partition between the solution and the solid phases [11]. In the available publications where the application of magnesium fertilizer (dolomite) have been recommended, the various authors made their recommendation based on agronomic soil test without considering the portion of fertilizer that might be adsorbed within the soil system. As recovery of ionic nutrients in applied fertilizer is typically only 15 to 20%, it is likely that, the major portion of the applied magnesium fertilizer is adsorbed (fixed) to soils at their adsorption sites. Hence, application of magnesium fertilizer based on only agronomic soil test without the due consideration of magnesium adsorption capacity of each soil will end up being a flaw. To this end, it became necessary to study the adsorption of magnesium in soils obtained from selected cocoa plantations in Southwestern Nigeria in order to determine the maximum adsorption and buffering capacity of each soil for magnesium cation.

2. MATERIALS AND METHODS

Soil samples were collected at a depth of 0-15 cm with soil auger from selected cocoa plantations in Owena, Ile-Ife, Ibadan, Ekiti and Bodo in the month of January, 2013. Fig. 1 shows the locations of sampling points on the map of Nigeria. The annual rainfall of the selected locations ranged from 1300 to 2000 mm. The sample collection was restricted to 15cm because most of the nutrients and organic matter are higher in concentration between 0 and 30 cm. The deeper you go in the soil profile, the lower the concentration of nutrient elements and organic matter. The soil samples were air-dried and sieved with 2 mm sieve prior to analysis.

2.1 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 Mg L^{-1} in 0.01M CaCl_2 solution was added to each sample. Three drops of toluene was added to prevent microbial activity. The soil samples were shaken on a mechanical shaker for 16 hours equilibration at 25°C. At completion, the equilibrated samples were centrifuged at 4,000 rpm and filtered with Whatman filter Paper No 1. The concentration of magnesium in the filtrate was determined with Buck Scientific Atomic Absorption Spectrophotometer (Buck 210). The quantity of magnesium adsorbed by each soil sample was

calculated from the difference between the concentration of magnesium in solution before and after equilibration. Data obtained from the experiment were fitted into Langmuir, Freundlich and Dubinin-Radushkevich equations to determine the various constants.

2.2 Physicochemical Analysis of Soil Samples

The pH values of the samples were determined in distilled water using a soil-solution ratio of 1:1 [12]. Organic carbon was determined by the Walkley-Black wet oxidation method [13]. Exchangeable basic cations were extracted with 1N ammonium acetate with K and Na determined by flame photometry while Ca, Mg, Fe, Zn, Al and Mn were determined with Buck Scientific Atomic Absorption Spectrophotometer [14]. Particle size distribution was determined by the hydrometer method after dispersion with sodium hexametaphosphate [15]. Available Phosphorus was determined using Bray and Kurtz method [16].

3. RESULTS AND DISCUSSION

3.1 Quantification of Magnesium Adsorption in the Studied Soils

The capacity of the various soils to retain magnesium was determined using equation 1

$$Q = \frac{V\Delta C}{w} \quad (1)$$

where Q is the quantity of magnesium adsorbed in mg kg⁻¹, V is the volume of solution added to the sample in liter, ΔC is the difference in Mg

concentration between the initial and the final concentration after equilibration ($C_o - C_e$); W is the weight of soil sample used in kilogram.

At initial solution concentration of 40 mg L⁻¹, soil obtained from Bodo had the least adsorbed magnesium while soil from Ibadan had the highest. With magnesium solution of 100 mg L⁻¹, soil obtained from Bodo had the lowest quantity of adsorbed Mg while soil from Owena had the highest value of adsorbed Mg.

Soil sample obtained from Bodo consistently had the lowest magnesium adsorption capacity under the experimental conditions except with 20 mg L⁻¹ initial manesium solution (Fig. 2). The low Mg adsorption demonstrated by soil obtained from Bodo is attributable to its physicochemical properties. Soil physicochemical properties (Table 1) shows that, Bodo soil had the least percent clay compared to the rest of the soil samples. Clay plays important role in the adsorption of cations in soil. It determines cations availability by nonspecific adsorption (exchange) [17,18]. The surface of an individual clay particle is negatively charged. Consequently, their surfaces attract and adsorb positively charged ions. Hence, increase in clay contents of soil provides more sites for adsorption [19]. Other factors that might have led to the low adsorption of Mg in Bodo soil as compared with the rest soils are the relatively lower pH, organic carbon and CEC. Table 1 shows that, Bodo soil had the least cation exchange capacity among the five soils studied. Cation exchange is the interchange between a cation on the surface of any negatively charged particle and those in soil solution.

Table 1. Physicochemical properties of the studied soils (mean of three replication \pm SD)

Parameters	Ile- lfe	Owena	Ekiti	Ibadan	Bodo
Ca (cmol/kg)	7.50 \pm 0.50	8.08 \pm 0.72	6.86 \pm 0.89	5.84 \pm 0.62	5.29 \pm 0.94
Mg (cmol/kg)	0.94 \pm 0.04	1.02 \pm 0.04	0.76 \pm 0.10	0.65 \pm 0.08	0.47 \pm 0.04
Na (cmol/kg)	0.24 \pm 0.02	0.21 \pm 0.01	0.20 \pm 0.06	0.26 \pm 0.05	0.22 \pm 0.06
K (cmol/kg)	0.22 \pm 0.01	0.43 \pm 0.03	0.35 \pm 0.07	0.42 \pm 0.03	0.33 \pm 0.03
Al (mg/kg)	0.60 \pm 0.05	0.36 \pm 0.02	0.24 \pm 0.04	0.56 \pm 0.08	0.24 \pm 0.04
Fe (mg/kg)	6.00 \pm 0.20	6.00 \pm 0.42	5.80 \pm 0.26	7.50 \pm 0.27	1.80 \pm 0.08
Mn (mg/kg)	6.48 \pm 0.32	2.64 \pm 0.02	0.60 \pm 0.07	3.86 \pm 0.69	2.28 \pm 0.07
Cu (mg/kg)	0.30 \pm 0.05	0.72 \pm 0.03	0.30 \pm 0.06	0.84 \pm 0.06	0.36 \pm 0.03
pH	6.69 \pm 0.45	6.85 \pm 0.72	6.72 \pm 0.74	6.70 \pm 0.45	6.60 \pm 0.30
Org. C (%)	1.74 \pm 0.05	1.96 \pm 0.03	1.53 \pm 0.05	1.84 \pm 0.07	1.44 \pm 0.02
CEC	8.90 \pm 0.06	9.74 \pm 1.02	8.17 \pm 0.63	7.17 \pm 0.21	6.31 \pm 0.20
Sand (%)	71.50 \pm 0.25	69.50 \pm 2.10	62.20 \pm 3.16	73.00 \pm 3.10	81.10 \pm 2.61
Silt (%)	11.30 \pm 0.09	17.30 \pm 1.05	14.60 \pm 1.38	14.00 \pm 1.02	6.30 \pm 0.92
Clay (%)	17.20 \pm 0.13	13.20 \pm 0.93	23.20 \pm 1.26	13.00 \pm 1.05	12.60 \pm 0.98

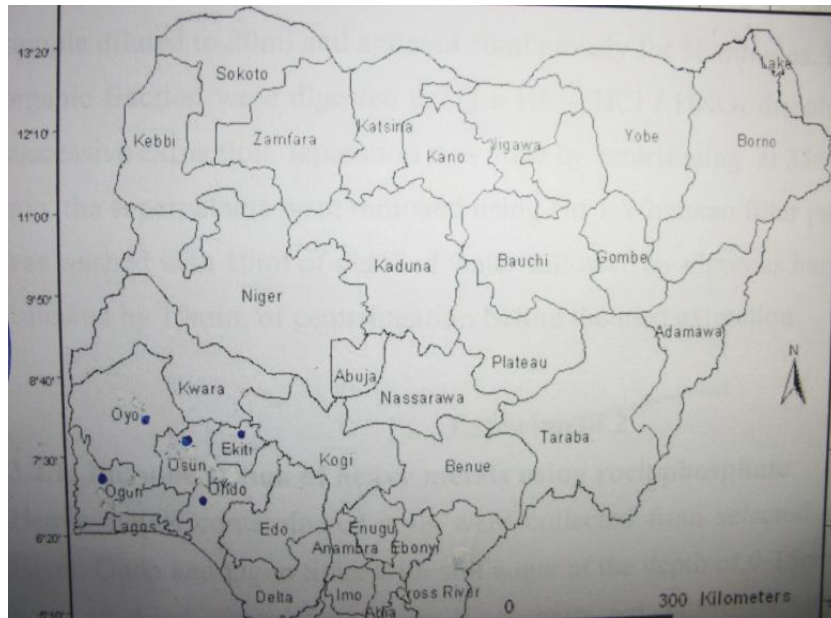


Fig. 1. Locations of sample collection on the map of Nigeria

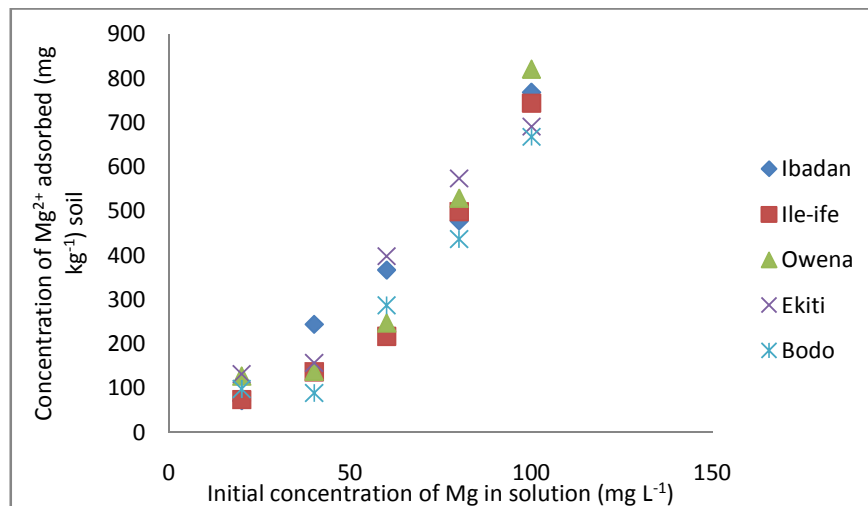


Fig. 2. Graphical relationship between solution and adsorbed magnesium

The negative charges responsible for cation-exchange capacities arise in three distinct ways (1) Cation substitution within mineral layers (2) Broken-edge bonds and (3) H⁺ ionizing from organic materials- carboxyl groups and phenolic group [20]. On the other hand, Owena soil which had the highest adsorption capacity for Mg was found to have the highest values of organic carbon (1.96%), CEC (9.74) and pH 6.85) (Table 1). These parameters collectively contributed to the comparative higher adsorption capacity in the soil compared with the rest soils.

3.2 Adsorption Isotherm

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The adsorption isotherm is important from theoretical and practical point of view. In order to understand the behavior and mechanism of magnesium adsorption in soil, it is important to establish the most appropriate sorption model that best describe the adsorption of the cation. The

parameters obtained from the different models provide important information on the adsorption mechanisms, the surface properties and affinities of the various soils for magnesium. The earliest and simplest known relationships describing the adsorption equation are the Freundlich and the Langmuir isotherms [21].

3.3 Langmuir Adsorption Isotherm

The theoretical Langmuir Isotherm [22] is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface [23]. In simple terms, Langmuir model is based on the assumption that, chemical ions are adsorbed at a fixed number of well defined sites; each site can hold only one ion; all sites are energetically equivalent and there is no interaction between the adsorbed ions.

The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants. It is equated by

$$\frac{C_{eq}}{q} = \frac{1}{(b \cdot q_{max})} + \frac{C_{eq}}{q_{max}} \quad (2)$$

From the linear plot of $\frac{C_{eq}}{q}$ Vs C_{eq} , the values of Langmuir constants were calculated in which q_{max} and b were obtained from the slope and intercept of the plots respectively. q_e is the amount of magnesium adsorbed per unit mass of the soil, b is the adsorption constant related to the enthalpy of adsorption, C_e is the equilibrium concentration of Mg and q_{max} is the maximum adsorption capacity. The maximum adsorption, ' q_{max} ' ranged from 5.38 to 21.74 mg g⁻¹ with a mean value of 12.75 mg g⁻¹. Sample obtained from Bodo had the least q_{max} while soil from Ibadan had the highest q_{max} value (Table 2). Though the Langmuir equation did not give a good fit for magnesium adsorption, result suggests that, soil obtained from cocoa plantation in Ibadan has the highest capacity to retain magnesium on homogenous surfaces compared with soils from Owena, Ekiti, Ile-Ife and Bodo.

3.4 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 [24]. The model is represented by the equation

$$q = K_f C_e q^{1/n} \quad (3)$$

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

$$\ln q = \ln K_f + 1/n \ln C_e \quad (4)$$

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 (Fig. 3). According to [25], n value between 1 and 10 represents beneficial adsorption. In the studied soils, the values of n ranged between 1.89 and 5.20 (Table 3). Data obtained suggest that, beneficial adsorption of Mg on heterogeneous sites took place in the course of adsorption. [26] reported that, exponent of the Freundlich equation ($1/n$) was independent of time and temperature but dependent of soil properties.

Table 2. Constants obtained from Langmuir Isotherm

Location	Equation	q_{max}	b	R^2
Ibadan	$y = -0.046x + 3.361$	21.74	3.36	0.61
Ile-Ife	$y = -0.106x + 6.844$	9.43	6.84	0.58
Owena	$y = -0.139x + 7.739$	7.19	7.74	0.67
Ekiti	$y = -0.050x + 3.58$	20.00	3.58	0.43
Bodo	$y = -0.186x + 11.20$	5.38	11.20	0.76
Mean		12.74	6.54	0.61
SD		7.576	3.24	0.12

Table 3. Freundlich isotherm constants

Location	Equation	K_f	n	R^2
Ibadan	$y = 0.530x + 1.840$	6.30	1.89	0.91
Ile-Ife	$y = 0.470x + 2.235$	9.35	2.13	0.77
Owena	$y = 0.192x + 3.097$	22.13	5.20	0.70
Ekiti	$y = 0.352x + 2.499$	12.17	2.84	0.77
Bodo	$y = 0.246x + 3.065$	21.43	4.07	0.94
Mean		14.27	3.226	0.81
SD±		7.162	1.391	0.10

The magnitude of ' n ' shows easy separation of Mg from solution while K_f shows adsorption capacity. K_f is also related to buffering capacity. The adsorption capacity K_f values ranged from 6.30 to 22.13. Owena soil had the highest value

while Ile-Ife soil had the least value. Similarly, Owena soil had the highest n value while Ibadan soil had the least n value. From agronomic point of view, Owena soil will retain more magnesium when equal fertilizer rate is applied on the five soils.

The high coefficient of determination R^2 in Freundlich isotherm is an indication that, the adsorption of Mg was on the heterogeneous sites with varying energies of adsorption. [27] Reported that, the adsorption of heavy metal in soils was on heterogeneous adsorption sites. [28] 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 and intensity respectively had positive correlation with calcium, clay, CEC and pH in the studied soils (Table 5). This suggests that, the intensity and rate of magnesium adsorption could be enhanced with increased Ca, CEC, clay and pH of the soils. [29] In their study on Zn retention in calcareous soils of central Iran, reported significant relationship between Freundlich K_f and percentage of clay, CEC and CCE. [30] reported significant correlation of Freundlich K_f with soil pH and clay but was not significantly correlated with CEC and organic matter. Reyhanitabar et al. [29] reported a significant relationship between Freundlich n and percent clay content of the soil.

3.5 Dubinin-Radushkevich Adsorption Isotherm

Dubinin-Radushkevich isotherm was applied to estimate the characteristics porosity of the soils and the apparent energy of adsorption. The model is presented according to [31] as

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

Where B_D is related to the free energy of sorption per mole of Mg as it migrates to the surface of soil particles from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constant related to the degree of Mg sorption on the soil surface.

The linear form of the equation is given as

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

In the above expression, q_e is the amount of Mg adsorbed (mg g^{-1}) at equilibrium per unit weight of soil, q_D is the maximum adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration of Mg in solution (mg L^{-1}). The Dubinin-Radushkevich model also assumes heterogeneous adsorption. The D-R isotherm is derived from the plots of $\ln q_e$ against $RT \ln(1 + 1/C_e)$. The values of q_D and B_D were obtained from the intercept and slopes of the graph respectively (Fig. 4).

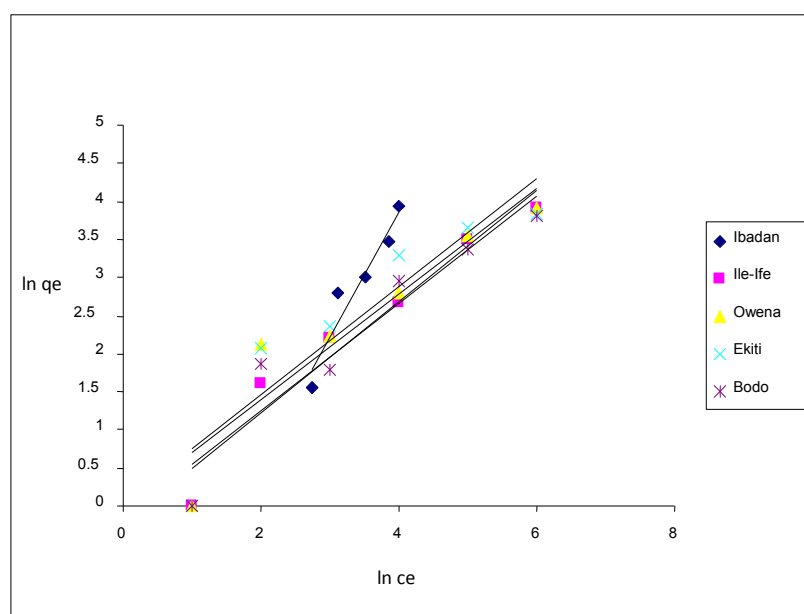


Fig. 3. Graphical representation of Freundlich isotherm

The Dubinin-Radushkevich constant q_D , ranged from 127 to 223 mg kg⁻¹ (Table 4). Owena soil had the highest magnesium adsorption capacity. This is in agreement with the result obtained from Freundlich equation. The constant B_D , relating to the free energy of sorption ranged from 0.002 - 0.007.

The Dubinin-Radushkevich parameters q_D and B_D had positive correlations with Ca, CEC, organic carbon and pH thereby indicating the influence of soil properties on porosity and free energy of magnesium adsorption in the soils. The findings of Hosseinpur and Dandanmozd, showed positive correlation of q_D with CEC in some calcareous soils of western Iran. [32] Reported increase in Mg adsorption with soil pH. At higher pH, negative charge of the soil increases thereby, providing increased number of exchangeable sites for divalent cations [33]. This offers explanation for the positive correlation between magnesium adsorption and pH in the present study. The mean free energy of adsorption (E) is defined as the free energy change when 1 mole of ion is transferred from solution to the surface of soil particles. E was calculated from B_D value using the equation.

$$E = \frac{1}{\sqrt{2B_D}} \quad (7)$$

The magnitude of E is useful for estimating the type of adsorption. If this value is in the range of 8-16 KJ mol⁻¹, the adsorption type is ion exchange [34] and if it is < 8 KJ mol⁻¹, then the adsorption is physical.

The E values calculated in this study ranged from 8.45 to 15 KJ mol⁻¹ (Table 4). Result showed that, Owena soil with the highest Mg adsorption had the least E value which implies that, the free

energy required for the transfer of 1 mol of Mg ion from solution to the surface of the soil was minimal in Owena soil compared with the rest of the soils investigated. This energy can be likened to the activation energy such that, the lower the activation energy, the faster the rate of reaction. The low E value in Owena soil might have contributed to the higher adsorption of Mg onto the soil surfaces (Table 4). This is based on the assumption that, lesser resistance (low transfer energy) to ionic flow in soil solution was encountered by magnesium in Owena soil compared with the remaining soils.

Table 4. Dubinin-Radushkevich constants

Location	q_D	B_D	E	R ²
Ibadan	164	0.003	12.91	0.96
Ile-Ife	177	0.004	11.18	0.90
Owena	223	0.007	8.45	0.93
Ekiti	127	0.002	15.00	0.97
Bodo	178	0.005	10.00	0.90
Mean	174	0.004	11.51	0.93
SD±	34.4	0.001	2.544	0.02

Correlation between E and soil physicochemical properties shows that, the free energy change (E) had negative correlation with CEC, pH, Ca, K, Mn and Cu (Table 5). By implication, an increase in CEC, pH, Ca, K, Mn and Cu may lead to the reduction of the free energy required to transfer 1 mole of magnesium from solution to the soil surface. The range (8.45 to 15 KJ mol⁻¹) of the free energy E suggests that, adsorption of magnesium in the selected cocoa soils in Southwestern Nigeria was controlled by ion exchange mechanism. This implies that, adsorbed magnesium can become available for plant uptake when the need arise.

Table 5. Correlation coefficients of Freundlich and Dubinin-Radushkevich constants and soil properties

Properties	Freundlich		Langmuir		Dubinin- Radushkevich		
	K_f	n	q_{max}	b	q_D	B_D	E
Calcium	0.101	0.272	0.187	-0.162	0.413	0.368	-0.256
Magnesium	-0.007	0.177	0.133	-0.221	0.434	0.348	-0.254
Sodium	-0.658	-0.652	-0.279	-0.237	0.035	-0.194	0.042
Potassium	0.234	0.404	-0.298	-0.236	0.236	0.231	-0.086
Aluminum	-0.686	-0.611	-0.195	-0.344	0.166	-0.091	-0.021
Iron	-0.680	-0.460	-0.664	-0.856	-0.078	-0.287	0.356
Manganese	-0.430	-0.44	0.210	0.057	0.313	0.117	-0.236
Copper	-0.079	0.111	-0.267	-0.281	0.442	0.292	-0.371
Organic C	-0.125	0.107	-0.56	-0.297	0.622	0.434	-0.560
Clay	-0.336	-0.338	-0.0452	-0.522	-0.733	-0.663	0.745
CEC	0.087	0.273	0.156	-0.192	0.436	0.379	-0.263
pH	0.183	0.430	-0.030	-0.299	0.485	0.431	-0.257

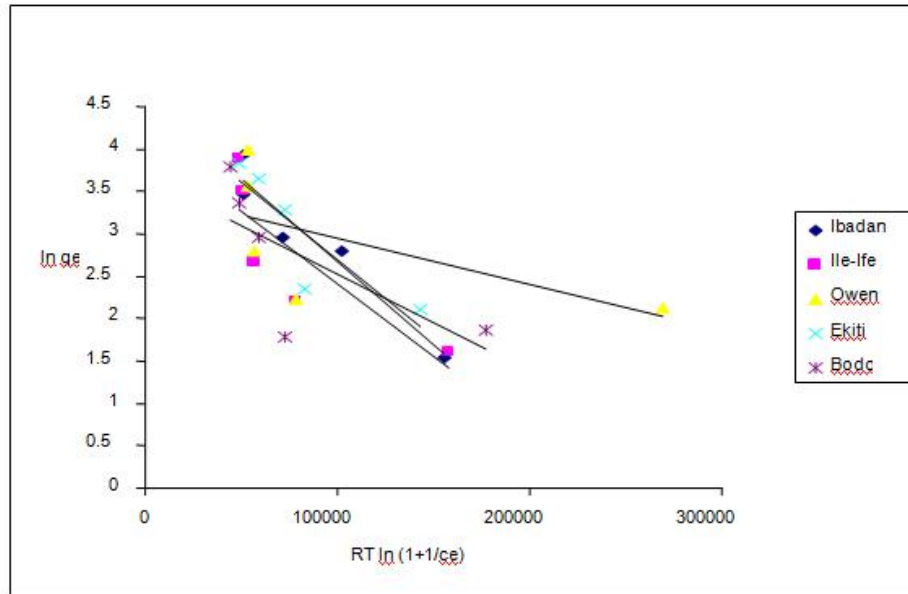


Fig. 4. Graphical representation of Dubinin-Radushkevich model

The inability of the Langmuir equation to describe magnesium adsorption in the studied cocoa soils suggests that, the sorption of magnesium was not on homogeneous adsorption sites. [35] Earlier reported the inability of Langmuir equation to describe the adsorption of Mg ions in three Malaysian rice soils.

Our findings from the study point to the fact that, the adsorption of magnesium in Ibadan, Ile-Ife, Ekiti, Owena and Bodo soils occur on heterogeneous surfaces with each adsorption site having its discrete energy.

4. CONCLUSION

The study showed that, Owena soil had the highest capacity to fix magnesium ions meaning that, more magnesium fertilizer will be required in Owena soil to give equal plant response to magnesium application compared with the rest soils. Adsorption of magnesium was best described by Freundlich model. Soil parameters that mainly influenced magnesium adsorption are clay content, cation exchange capacity, organic matter and pH.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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