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Evaluation of Some Chemical Properties of Geheku Clay Deposit in Kogi State, Nigeria for Possible Application as Soil Blends

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ABSTRACT

Geheku clay deposit in Kogi State, Nigeria was evaluated for its nutrient content in order to mitigate the problem of the decline in arable land which has been amplified by increase in population and urbanization in Nigeria. Exchangeable cations (EC), cation exchange capacity (CEC), exchangeable acidity (EA) and percent base saturation which are indices of soil fertility were evaluated for the top (L_1) and bottom levels (L_2) of Geheku clay at different pH levels. These parameters were evaluated against pH 4, 6, 7 and 9 to establish the best pH where the essential nutrients will be available for plant uptake. Exchangeable Na^+ cations had the highest value at pH 9 for both levels recording values of 3.57± 0.09 cmol/kg and 3.38± 0.16 cmol/kg for L_1 and L_2 respectively. Exchangeable K^+ ion was highest at pH 4 in both cases while Mg^{2+} was highest at pH 4 and 5 for L_1 and L_2 respectively. Ca^{2+} cations were highest at pH 4 and pH 7 for L_1 and L_2 respectively. The Ca/Mg ratio was greater than 4 for both layers indicating that the clay is well-structured. The fertile nature of the clay material was evident from the high values of CEC obtained at each pH with the highest values of 11.42± 1.12 and 12.73± 0.72 cmol/kg obtained at pH 7 for L_1 and L_2 respectively. However, the percent base saturation was highest at the acidic pH5 for both layers and also reasonably high at the alkaline pH of 9. Thus, depending on crop tolerance to acidity or alkalinity, a blend of Geheku clay at either pH 5 or 9 with nutrient improvised soil is recommended for optimum nutrient availability for plant uptake and effective soil management.

Keywords: Cation exchange capacity, Exchangeable cations, Geheku clay, Soil nutrients

INTRODUCTION

Nigeria is the most populous country in Africa with an estimate of over two hundred million (Yahaya *et al.*, 2020). The rapid growth in population demands high level of food security for the sustenance of human life. However, the demands for shelter in rural areas, urbanization coupled with environmental issues which are fallouts of population pressure is gradually creeping into arable land otherwise used for farming (Ifatimehin *et al.*, 2009). As a result, the surge in the demand for food will likely lead to a decline in agricultural produce in the foreseeable future as more pressure are being exacted on the diminishing arable land for crop production. Over-burdening of soils due to bad agricultural practices and improper land use have been attributed to erosion and loss of soil nutrients needed for optimum crop yield (Fu *et al.*, 1999; Gong *et al.*, 2006; Mafongoya *et al.*, 2006; Alavaisha *et al.*, 2019). Appropriate measures are now being implemented to avoid this catastrophe. Some of which includes; amending soils depleted of its nutrients with fertilizers, animal dungs and agricultural waste (Eneji *et al.*, 2001; Omoruyi *et al.*, 2016; Okenmuo *et al.*, 2018). Another potent method is the blending of nutrient impoverished soils with clay rich in nutrient elements (Sheemeen and Petra, 2017).

Soil fertility can be best described as ability of the soil to hold nutrients in the right proportion to aid plant growth (El-Seedy, 2019). Soil nutrient elements that encourage plant growth are mostly present in the soil as cations. These cations are positively charged ions which includes potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na^+), ammonium (NH_4^+), iron (Fe^{2+}), hydrogen (H^+),manganese(Mn^{2+}), zinc (Zn^{2+}), copper (Cu^{2+}) and aluminum (Al^{3+}) with Ca, Mg and K being the most essential elements to plants (Uchida, 2000; Hazelton and Murphy, 2007). The ability of soils to hold these cations is a function of the abundance of clay minerals and organic matter it contains (Martel *et al.*, 1978; Emmanuel *et al.*, 2018). Clay materials and organic matter are sources of negative charge pool that binds these cations in soils through electrostatic forces. Therefore, the amount of cationic nutrients present in soils for plant uptake is influenced by the amount of negative binding sites on clay minerals /organic matter present in the soils. Clay minerals are abundant naturally occurring fine-grained materials which become plastic at appropriate water content and harden when fired or dried (Akhirevbulu *et al.*, 2010). Chemically, they are composed of hydrous aluminum phyllosilicates arranged in either an octahedral and/or a tetrahedral geometry to form individual layers or sheets interlayered with cations (Lainé *et al.,* 2017). The arrangement or composition of the octahedral and tetrahedral sheet accounts for the physical as well as chemical properties of the clay material. Generally, no two clay deposits have exactly the same chemical and physical properties, its properties are derived from the parent material (Rashidi and Seilsepour, 2008; Aboudi Mana, *et al.*,2017). Cation exchange capacity (CEC) is one of the most important indicators that determine soil fertility (Liang *et al.*, 2006; Olorunfemi *et al.*, 2016). It is a measure of the ability of the soil to hold its cations and also exchange them in the presence of other cations particularly ammonium (NH_4^+) ion from fertilizers (Ogeleka *et al.,* 2017). These exchangeable cations (K^+, Na^+, $Mg^{2+}$and Ca^{2+}) also referred to as exchangeable bases are essential nutrients of plant. Therefore, soils with high CEC levels can be said to be fertile especially if saturated with exchangeable bases, while those with relatively low CEC are thought to be infertile and, in most cases, unable to support plant growth (Ogeleka *et al.,* 2017). To this end, we set out to investigate the fertility of Geheku clay deposit found in Kogi state located in north central Nigeria commonly referred to as the middle belt.

The state is known for its rocky terrain and huge mineral deposit. It equally has a large clay deposit most of which is explored in the production of ceramics and architecture (Akhirevbulu *et al.,* 2010; Bamidele, 2018). Manukaji (2013) reported the use of Kogi clay as a potential insulating material, while a more recent study focused on the exploration of this clay material in the production of fertilizers (Bamidele, 2018). Our group recently examined and reported the physico-chemical and mineralogical properties of Geheku clay deposit (Irabor and Okunkpolor, 2020). In this study, the cation exchange capacity (CEC), exchangeable cations (EC), exchangeable acidity (EA) and percent base saturation of Geheku clay deposit were evaluated with a view of establishing the clay nutrient and also to ascertain if this clay material can be used directly as a soil blend with soil deficient of soil nutrient. Since it has been reported that most of these parameters are influenced by a subtle change in pH (Gray *et al.*, 2016; Khaledian *et al.*, 2017), the analysis were performed at different pH values to obtain the best condition for which a blend of these clay with non-fertile soils can lead to optimum nutrient availability for effective soil management.

MATERIALS AND METHODS

Sampling Method and Location

Representative clay materials were obtained from Geheku in Kogi state with coordinates between latitude 8^o 19’ 26”N and longitude 6^o 52’ 47”E as depicted in Figure 1. Representative samples of Geheku clay beds were collected from two depths coded L_1 and L_2 between the ranges of 0 –1.9 and 1.9 - 3.8 m from top to bottom**,** respectively. The excavation and collection of the samples were done with the aid of digger, measuring tape, stainless steel shovel and hand trowel. The sampling of the materials was also based on colour variation in line with Onyeobi *et al.*, 1994.

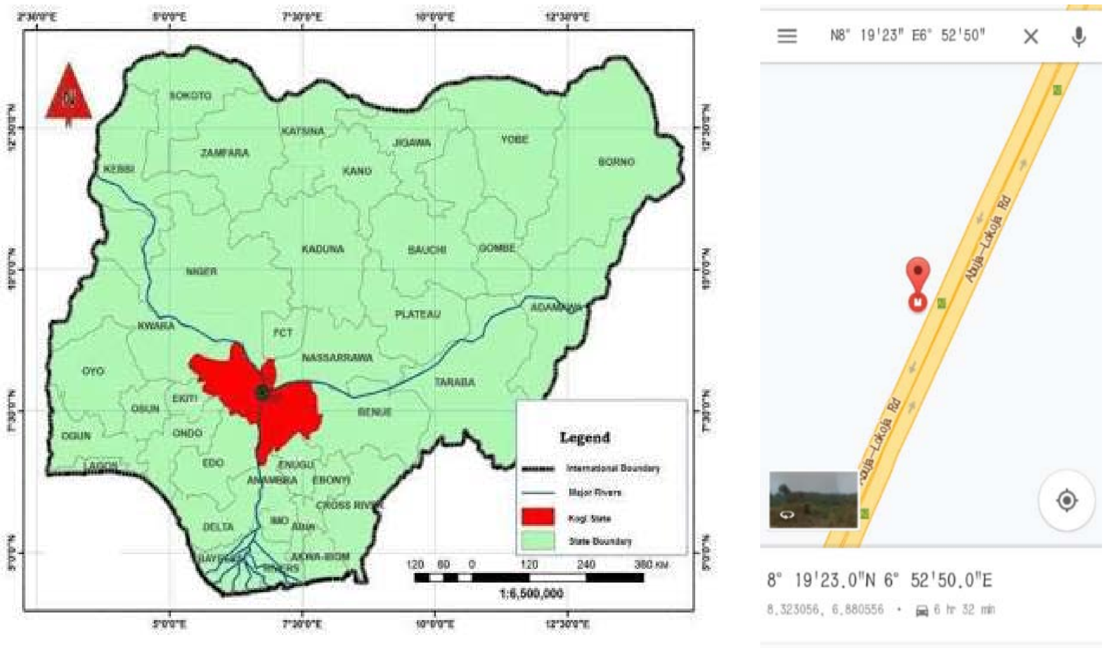

Figure 1: Location of sample site (Olarewaju *et al.*, 2014).

MATERIALS AND METHODS

All regents were either purchased from Honeywell Fluka or BDH chemicals and used as received. Deionized water was used in all cases unless otherwise stated. The solutions containing exchangeable Ca^{2+} and Mg^{2+} were analyzed using atomic absorption spectrophotometer (AAS) Bulk Scientific 210VGP model. Solutions of exchangeable K^+ and Na^+ were analysed using flame emission (FE) spectrophotometer Sherwood 410 model. Estimation of cation exchange capacity (CEC) was performed on a Jenway UV-Vis spectrophotometer 6051 model. All analyses were carried out in triplicates with corresponding mean and standard deviation calculated. Results are expressed in mean values with their corresponding standard deviations.

Sample preparation/Analysis

The samples collected were air dried at room temperature and prepared for testing by grinding with a ceramic pestle and mortar. Thereafter, the samples were pulverized to its powdery form and then filtered through 2.00 µm sieve. Finally, the samples were activated at 400 °C for 3 hours in a muffle furnace.

Following the method reported in literature (Chimdi *et. al.*, 2012; Irabor *et al.*, 2020), the estimation of exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) at a netutral pH of 7, was performed by reacting 25 g of the pretreated clay sample with 125 mL ammonium acetate (1.0 M NH_4OAc) in a beaker. The beaker was covered with an aluminium foil and agitated 3 hours daily on a mechanical shaker for 3 days and thereafter the mixture was allowed to stand. The clay-NH_4OAc mixture was filtered under vacuum using Whatman paper No. 1 and the residue washed with NH_4OAc (25 mL *x* 4). The leachates were combined in a 250 mL volumetric flask which was made to mark with 1.0 M NH_4OAc for EC analysis (Ca^{2+}, Mg^{2+}, K^+, Na^+) using either an AAS or flame photometer.

For the estimation NH_4^+ the same procedure was followed but with further washing of clay residue with 95% ethanol (25 mL *x* 6) to remove excess NH_4OAc. To leach out the adsorbed NH_4^+ in the clay, the residue was then washed with 1 M KCl (5 × 25 mL). The leachate from KCl washings were added up in 250 mL volumetric flask and made up to mark by adding 1.0 M KCl. NH_4 was determination using a colorimeter (Jenway 6051) which was read at 636 nm (Baethgen and Alley, 1989).

Exchangeable acidity (EA) values were obtained from the subtraction of concentrations of the sum of the exchangeable cations (Na, K, Mg and Ca) from the cation exchange capacity (CEC) as shown in equation 1, while the percent base saturations were calculated using the expression reported by Yemir and co-workers (2006) as shown in equation 2.

$$\mathrm{E.A.} = \mathrm{CEC} - (Na^+ + K^+ + Mg^{2+} + Ca^{2+}) \ldots\ldots (1)$$

$$\%\,BS = \frac{[Na^+ + K^+ + Mg^{2+} + Ca^{2+}]}{CEC} \times 100 \ldots. (2)$$

Depending on the pH of interest for the analysis (pH4, pH5 or pH9); 25 g of the activated clay samples were first subjected to either an acid or alkaline media for seventy-two (72) hours and mechanically agitated for 3 hours daily as previously described by Irabor and co-workers (2020). For the estimation at pH 4, clay samples were initially treated with 0.1 M HCl and 0.1 M potassium hydrogen phthalate (KHP) buffer 4 solution for 72 hours. Intuitively, at this pH, it is expected cations that could not be held by the clay material will be leached into the buffer solution. The clay-buffer solution was filtered and then washed with deionized water before subjecting to the procedure for EC and CEC described above. In like manner, estimations at pH 5 and pH 9 were performed using 0.1 M NaOH/ 0.1 M KHP and 0.025 M Borax/ 0.1 M HCl buffer solutions, respectively. EA and percent BS were also estimated as previously described using equations 1 and 2 respectively.

RESULTS AND DISCUSSION

From physical observation, top clay material L_1 obtained from Geheku was light yellow in colour while the bottom level L_2 was grey in colour, an indication that both layers may not have the same physiochemical properties (Osunade 1992; Aitkenhead *et al.*, 2013). The investigation of exchangeable cations (Na, K, Mg and Ca), cation exchange capacity, exchangeable acidity, and percent base saturation at different pH values on Geheku clay sample L_1 and L_2 obtained from Kogi state are summarized in Tables 1 and 2 respectively. For Geheku clay sample L_1, the monovalent exchangeable cations, the values for sodium ranged from 0.51± 0.03 to 3.57± 0.09 cmol/kg, while that of L_2 ranged from 0.62± 0.01 to 3.38± 0.16 cmol/kg. For both layers (L_1 and L_2), the highest sodium cation values of 3.57± 0.09 and 3.38± 0.16 cmol/kg respectively, were recorded at pH 9. The amount for potassium cations present in both layers of the clay samples were significantly high at all pH values, with the highest value of 1.85±0.43 and 1.86±0.32 cmol/kg recorded at an acidic pH of 4 for L_1 and L_2 respectively. High levels of K^+ in soils have been reported to enhance photosynthesis rate, plant growth, yield and drought resistance in different crops under water stress conditions (Sharma *et al.*, 1996; Tiwariet *et al.*, 1998; Egila *et al.*, 2001). Therefore, this study is significant as it reveals that Geheku clay can be used for the aforementioned purposes.

Table 1: Result of Exchangeable Cations (Na, K, Mg and Ca), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Percent Base Saturation obtained at different pH of Geheku clay top layer (L_1)

Parameters	**pH4**	**pH5**	**pH7**	**pH9**
Na (cmol/kg)	0.51± 0.03	2.96± 0.05	0.53± 0.10	3.57± 0.09
K (cmol/kg)	1.85± 0.43	1.47± 0.04	0.68± 0.09	0.28± 0.08
Mg (cmol/kg)	0.19± 0.02	0.18± 0.02	0.13± 0.03	0.15± 0.02
Ca (cmol/kg)	0.80± 0.04	0.82± 0.02	1.04± 0.03	0.93± 0.26
CEC (cmol/kg)	6.12± 1.78	7.06± 0.28	11.42± 1.12	6.63± 1.41
EA (cmol/kg)	2.77	1.63	9.04	1.70
Percent Base saturation (%)	54.73	76.93	20.82	74.45

Table 2: Exchangeable Cations (Na, K, Mg and Ca), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Percent Base Saturation (PBS) obtained at different pH of Geheku clay bottom layer (L_2**)**

Parameters	**pH4**	**pH5**	**pH7**	**pH9**
Na (cmol/kg)	0.62± 0.01	2.94± 0.17	0.75± 0.24	3.38± 0.16
K (cmol/kg)	1.86± 0.32	1.57± 0.15	1.16± 0.06	0.52± 0.05
Mg (cmol/kg)	0.11± 0.04	0.14± 0.02	0.10± 0.04	0.07± 0.02
Ca (cmol/kg)	2.24± 0.23	1.53± 0.17	1.63± 0.18	1.41± 0.08
CEC (cmol/kg)	5.47± 2.84	6.76± 0.93	12.73±0.72	6.43± 0.10
EA (cmol/kg)	0.64	0.57	9.06	1.06
Percent Base saturation (%)	88.28	91.51	28.61	83.55

The values of exchangeable magnesium (Mg^{2+}) cations ranged between 0.13± 0.03 – 0.19± 0.02 cmol/kg and 0.07± 0.02 – 0.14± 0.02 cmol/kg for L_1 and L_2 respectively. Whereas the highest value in L_1 was obtained at pH 4 (0.19± 0.02 cmol/kg), the highest value of Mg^{2+} in L_2 was obtained at pH 5 (0.14± 0.02 cmol/kg). The values of Mg^{2+} obtained in both layers did not follow a clearly defined pattern with changes in pH through high acidity yielding higher values than the neutral and alkaline media. The exchangeable calcium (Ca^{2+}) ranged between 0.80± 0.04 – 1.04± 0.03 cmol/kg and 1.41± 0.08 – 2.24± 0.23 cmol/kg in L_1 and L_2 respectively. The values of exchangeable Ca^{2+} varied with pH in the following order: neutral > alkaline >acidic media for L_1, thus the lowest value was recorded at pH 4. In contrast, the highest value of 2.24± 0.23 cmol/kg for exchangeable Ca^{2+} was obtained at pH 4 in layer L_2. The values of exchangeable Ca^{2+} decreased steadily with increase in pH from the acidic to the alkaline region except for the neutral pH of 7 where a small spike in Ca^{2+} concentration was observed. The relationship between the ratio of exchangeable calcium ion to magnesium ion (Ca/Mg) when ≥ 1 influences soil property (Osemwota *et al.*, 2007; Salihaj and Bani, 2018). Some of these properties includes soil structures, water penetrations/drainage, root development and ultimately plant growth (Hazelton and Murphy, 2007; Osemwota *et al.*, 2007; Ostrowska and Porebska, 2017).

Our analyses for Geheku clay at the different pH levels revealed a Ca/Mg ratio ≥ 4, indicative of a well-structured soil type. Furthermore, the exchangeable cations (K^+, Mg^{2+} and Ca^{2+}) which are part of the essential nutrients of plant were found to be in sufficient amount in Geheku clay. The cation exchange capacity (CEC) values for L_1 ranged between 6.12 ± 1.78 – 11.42± 1.12 cmol/kg, whereas its value for L_2 ranged from 5.47± 2.84 – 12.73± 0.72 cmol/kg. The highest CEC value in both instances was obtained at a neutral pH. Although the CEC value for L_2 was slightly higher than L_1, the levels in both layers are sufficiently high enough to support plant growth. Since it has been well established that soil fertility shows a direct proportionality to CEC values as it indicates the ability of the soil to hold cations, the high CEC values obtained at pH7 suggests that the desired plant nutrients (exchangeable cations) are more readily available for plant uptake at this pH. However, at the neutral pH of 7 our findings revealed both layers of Geheku clay were saturated with the undesired acidic hydrogen (H^+) and aluminium (Al^{3+}) cations than the desired base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) with values of 9.04 and 9.06 cmol/kg obtained for L_1 and L_2 respectively. The values of exchangeable acidity (EA) varied with pH in the following order: neutral > alkaline > acidic for both layer of Geheku clay. Thus, the relationship between CEC and the EA was established to ascertain the best pH at which the exchangeable bases will be predominant in both layers of the clay. This relationship is represented graphically in Figures 1 and 2.

For both L_1 and L_2, it was observed that at a slightly acidic and alkaline media with moderately high CEC values, the presence of acidic cations relative to the base cations were minimal as depicted in Figures 2 and 3, respectively. From the figures, it can be inferred that pH5 is the best condition for optimal base cations availability for L_1 and L_2.As expected, the low values of EA at this pH, resulted in a very high percent base saturation of 76.93% and 91.51% for L_1 and L_2 respectively. This confirms that at pH5, the negative sites of the clay material are populated by more of the desired base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}).

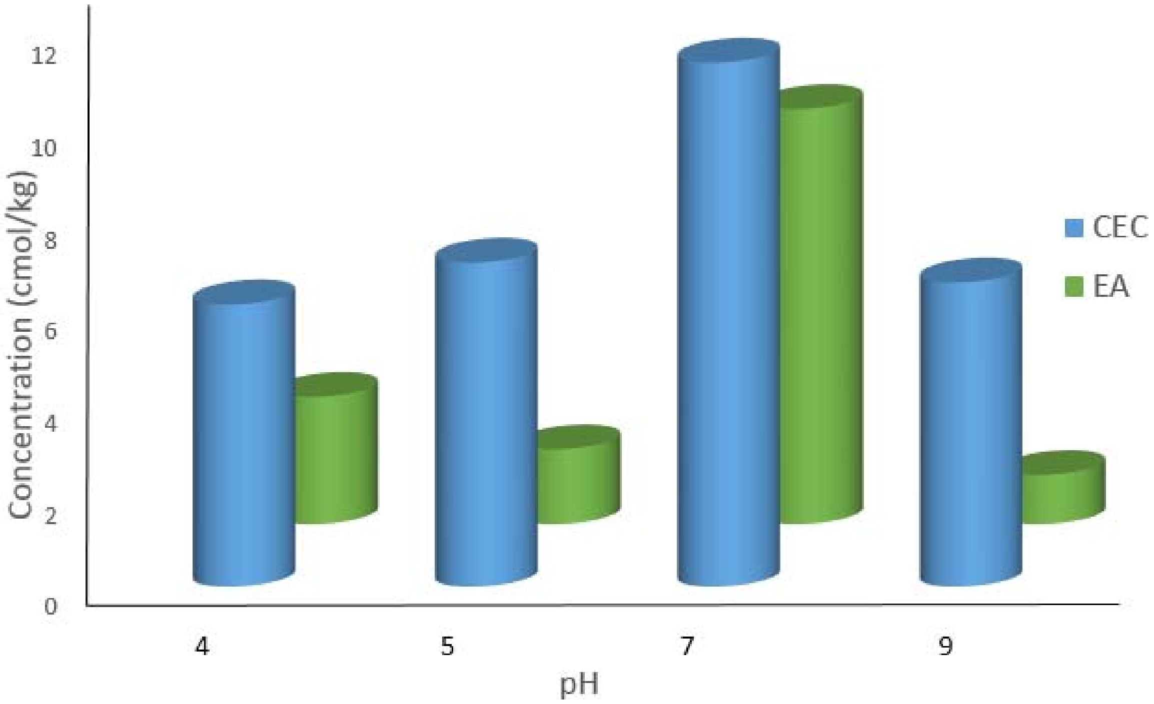

Figure 2: The relationship between cation exchange capacity (CEC), exchangeable acidity (EA) and change in pH for the top layer (L_1) of Geheku clay**.**

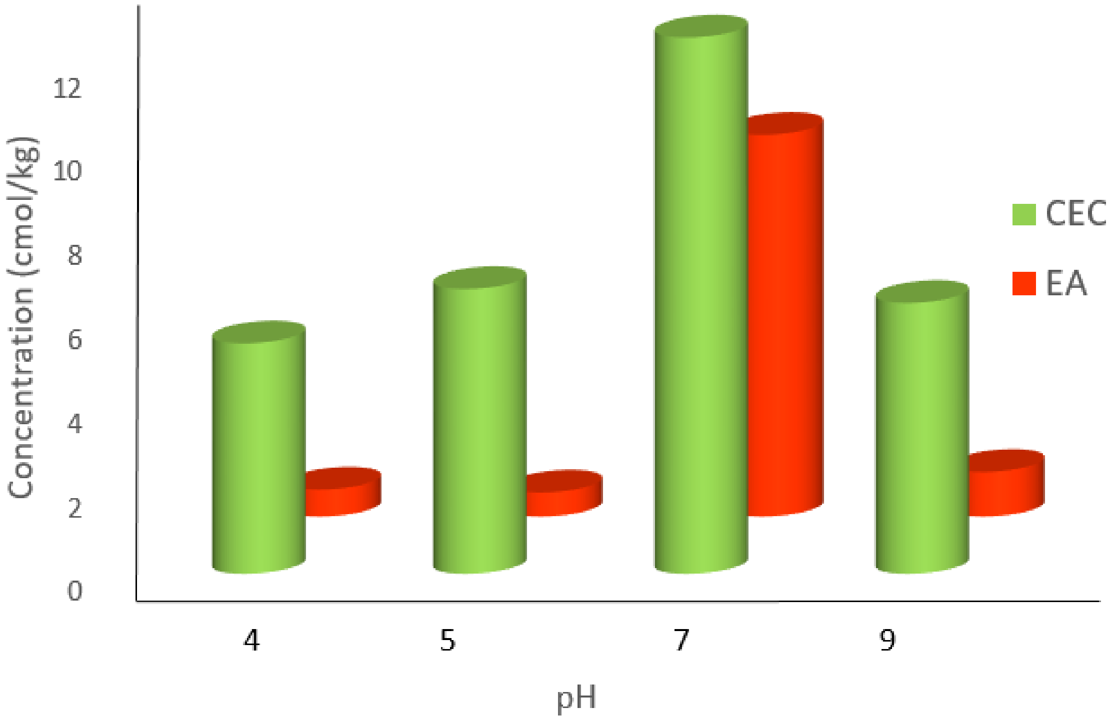

Figure 3. The relationship between cation exchange capacity (CEC), exchangeable acidity (EA) and change in pH for the bottom layer (L_2) of Geheku clay.

Interestingly, the base saturations showed an irregular but similar variation pattern with changes in the pH of the clay material for L_1 and L_2 (Figure 4). The lowest percentage base saturation of 20.82% and 28.61% was recorded at the neutral pH of 7 for L_1 and L_2, respectively. The values for percent base saturation followed the order pH5> pH9 > pH4 >pH7 for L_1, while that of L_2 was pH5> pH4 > pH9 >pH7. Overall, the bottom layer of Geheku clay had the highest percent base saturation at the different pH values in comparison with the top layer L_1. High percent base saturation implies that the negative sites of the clay material were occupied by exchangeable base cations. Thus, maintaining a soil blend with Geheku clay at a slightly acidic pH (pH5) or alkaline pH (9) will lead to optimum availability of plant nutrient. Moreso, at the pH values, the CEC levels are considerably high, therefore the clay fertility is not compromised.

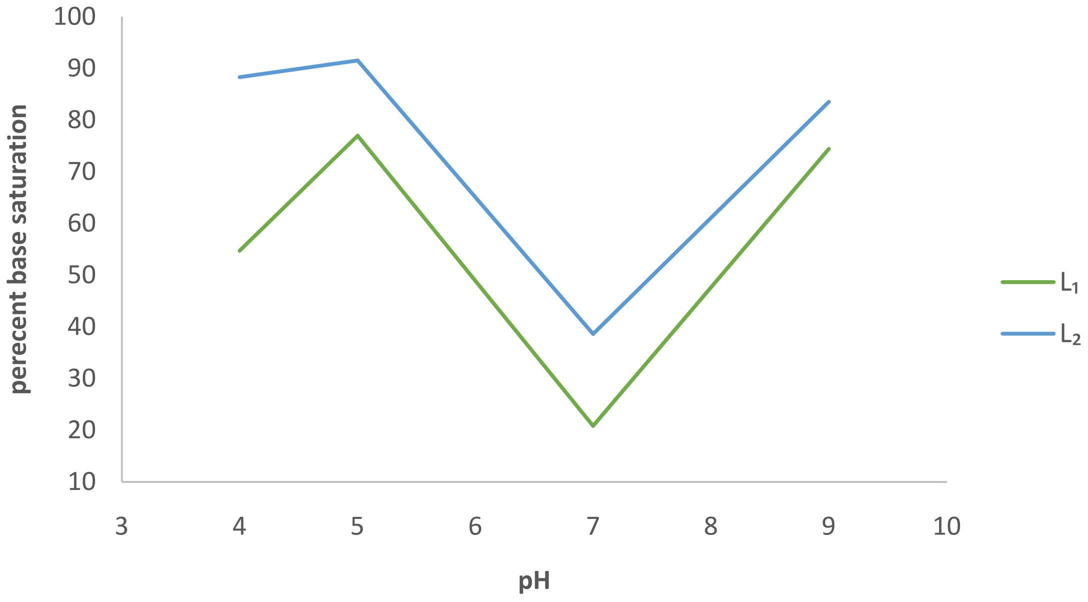

Figure 4: The relationship between pH and percent base saturation for the top layer (L_1) and bottom layer (L_2) of Geheku clay.

CONCLUSION

The exchangeable cations (EC), cation exchange capacity (CEC), exchangeable acidity (EA) and percent base saturation in relation to pH values for the top (L_1) and bottom (L_2) layers of Geheku clay deposit obtained in Kogi State, Nigeria was studied. Our study revealed that whereas, the exchangeable cations varied with pH, the CEC had optimum values at pH7 for both layers. The Ca/Mg ratio at each pH was greater than 4 for both layers indicating that the clay is well-structured. The percent base saturation was highest at the acidic pH5 for both layers and also reasonably high at the alkaline pH of 9. Therefore, a blend of this clay with any nutrient impoverished soil at either of this pH value (depending on crop tolerance to acidity or alkalinity) is recommended for optimum nutrient availability for plant uptake and effective soil management.

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