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# EVALUATION OF THE AVAILABLE PLANT NUTRIENTS AT DIFFERENT pH LEVELS OF AHOKOR CLAY DEPOSIT LOCATED IN KOGI STATE, NIGERIA.

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## ABSTRACT

The nutrient level of Ahokor clay deposit in Kogi State, Nigeria was evaluated with the view of using it as a soil ammendments in soils deficient in plant mineral nutrients. Exchangeable bases (EB), cation exchange capacity (CEC), exchangeable acidity (EA) and percent base saturation were determined at five different pH levels for the top (LT) and bottom layers (LB) of the clay. These parameters were determined at pH4, pH5, pH7, pH8 and pH9 respectively. The exchangeable bases varied with change in pH with optimum values of $K^+$ (1.120$\pm$0.300 cmolKg$^{-1}$) and $Na^+$ (0.701$\pm$0.010 cmolKg$^{-1}$) for LT obtained at pH7 and pH4 respectively, while those of $Ca^{2+}$ (0.920$\pm$0.025 cmolKg$^{-1}$) and $Mg^{2+}$ (0.298$\pm$0.027 cmolKg$^{-1}$) were recorded at pH9. Optimum values for the exchangeable bases for the bottom clay (LB) were recorded at pH9 with values of 0.536$\pm$0.020 cmolKg$^{-1}$, 3.522$\pm$0.023 cmolKg$^{-1}$, 1.959$\pm$0.020 cmolKg$^{-1}$ and 0.358$\pm$0.036 cmolKg$^{-1}$ recorded for $Na^+$ , $K^+$, $Ca^{2+}$ and $Mg^{2+}$ respectively. The optimum condition for application as soil ammendment was obtained at pH9 as the percent base saturation which indicates that the crystal lattice is occupied with more of the desired base cations was highest at this pH for both layers.

**Keywords**: Exchangeable bases, cation exchange capacity, exchangeable acidity, perecent base saturation, soil fertility.

## INTRODUCTION

Clay is a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired [1]. Their particle sizes are less than 2 micrometers with negative charge sites capable of attracting cation within the soil [2]. From a chemical standpoint, clay can best be described as a hydrous aluminosilicate complex material arranged in well-defined octahedral and tetrahedral geometries resulting in closely packed layers or sheets [3,4]. Depending on the parent material of the clay, the surfaces of the alumino-silicate sheets may consist of either the oxygen anions and/or the hydroxyl ions organized into a closely packed hexagonal network. These anionic frameworks are neutralized by exchangeable bases (cations) held together by electrostatic force in their crystal lattice [5].

When clay is dispersed in water, the clay mineral ionizes and these ions are hydrated or solvated by water molecule in a process generally referred to as swelling [1]. Research has shown that the degree of swelling is largely dependent on the nature and amount of exchangeable bases (also reffered as exchangeable cations) present in the crystal lattice of the clay [6–8]. On the basis of this, clay have been classified as swelling (montmorillonite) and non-swelling (kaolinite) clay [9–11]. Furthermore, clay exhibit other properties such as shrinkage on drying or firing, firmness, colour retention hardness, cohesion etc. For these reasons, most clay deposits in Nigeria are widely mined for wide range of applications in different sectors of the economy. In the manufacturing industries, they are employed for products such as ceramics, glass, adhesives, paints, insulators etc [12–15]. In the oil and gas sector, clay is employed in drilling muds and in some cases as catalyst for petroleum cracking. In the agricultural sector they are employed in the manufacturing of fertilizers and in remediation of contaminated soils [16–18]. In whatever sector they are employed what is key to their application is an appreciable knowledge, information and under-standing of the chemical composition as well as mineralogy of the clay deposit. Thus in the agricultural sector, a vast body of literature exists on the cation exchange capacity (CEC) of clay which has fostered its application in remediation studies particularly in heavy metal clean ups [19–22]. However, there is a dearth of information on the direct application of clay on soil deficient of mineral nutrient to improve the soil fertility despite the fact that the crystal lattice of clay holds sufficient amount of the essential plant nutrients in the form of cations. For this to become a common practice, a good evaluation of exchangeable bases (EB) and cation exchange capacity of the clay deposits which are clearly indices of soil fertility as well as an understanding of factors such as pH that can influence their availability is necessary. Therefore in this study, soil fertility indices such as; the cation exchange capacity (CEC), exchangeable bases (EB), exchangeable acidity (EA) and percent base saturation of Ahokor clay deposit found in Kogi State Nigeria were evaluated to establish if this clay material can be used directly as a soil ammendment in soils showing nutrient deficiency. The evaluation was carried out at different pH levels with a view of establishing the best pH for optimum release of the clay mineral nutrient for possible plant uptake.

## EXPERIMENTAL

### General information

All regents and solvents 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 exchangebale $Ca^{2+}$ and $Mg^{2+}$ were analyzed using atomic absorption spectrophotometer (AAS) Bulk Scientific 210VGP model. Solutions of exchangebale $K^{+}$ 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. Exchangeable acidity (EA) and percent base saturation were mathematically determined using expressions 1 and 2 respectively.

$$\mathrm{EA} = \mathrm{CEC} + (\mathrm{Na^{+}} + \mathrm{K^{+}} + \mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}) \text{.............(1)}$$

$$\%\, Base\ saturation = \frac{(\mathrm{Na^{+}}+\mathrm{K^{+}}+\mathrm{Mg^{2+}}+\mathrm{Ca^{2+}})}{100} \times 100 \text{ .....(2)}$$

Each experimentation was conducted in triplicate with corresponding mean and standard deviation calculated. All results were expressed as mean values with standard deviations.

### Sampling method / sample preparation

Samples were obtained from a clay mineral deposit in Ahokor, Kogi state which is located in North Central Nigeria. Sampling of the clay materials into layers was based on colour variation in accordance with Uduji and co-workers [23]. The samples were air dried at room temperature, then pulverized mechanically afterwards, it was sieved using a 2 μm sieve and activated in a Gallenkamp muffle furnace at 400 $^{o}$C for 3 hours. The activated clay samples were subjected to different acid and alkaline media treatment for seventy two (72) hours, mechanically agitated for at least three (3) hours a day. Thereafter, the various parameters were determined viz cation exchange capacity (CEC), exchangeable bases (EB), exchangeable acidity (EA) and percent base saruration.

## Chemical analysis

### Exchangeable bases (EB) and cation exchange capacity (CEC)

The exchangeable bases ($Ca^{2+}$, $Mg^{2+}$, $K^{+}$, $Na^{+}$) and cation exchange capacities were determined following literarure methods [24–27]. To a clean 250 mL beaker was added 25 g of the pretreated clay sample and 125 mL ammonium acetate ($NH_4OAc$) at pH7, the beaker was sealed with an aluminium foil . The mixture was agitated 3 hours daily on a mechanical shaker and allowed to stand for 3 days. Thereafter, clay-$NH_4OAc$ mixture was filtered through a Buchner funnel fitted with Whatman paper No. 1 under vacuum. The clay residue was then gently washed with $NH_4OAc$ (4 × 25 mL). All leachates were combined in a 250 mL volumetric flask and made to mark with 1 M $NH_4OAc$ for elemental analysis ($Ca^{2+}$, $Mg^{2+}$, $K^{+}$, $Na^{+}$) using instruments already mentioned above.

The residual clay sample was further washed with 95% ethanol (6 × 25 mL) to remove excess

$NH_4OAc$ and finally washed with 1 M KCl (5 × 25 mL) to leach the adsorbed $NH_4^+$ in the clay. Leachate from KCl washings were added up in 250 mL volumetric flask and made to volume by 1 M KCl for $NH_4$ determination in a colorimeter (Jenway 6051) at 636 nm according to Baethgen and Alley [26]. The same procedure was adopted for the other aqueous media with pH 4, 5, 8 and 9 respectively. For determinations at pH4, the clay sample was first treated with 200 mL of 0.1M HCl and 0.1 M potassium hydrogen phthalate (KHP) buffer 4 solution for 72 hours [28]. In like manner, estimations at pH5 were performed using 0.1M NaOH/ 0.1M KHP buffer system while determi-nations at pH8 and pH9 were achieved using 0.025M disodium tetraborate/ 0.1M HCl buffer systems as decribed by Ribbison and stoke [28].

## RESULTS AND DISCUSSION

The results for the exchangeable bases ($Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$), cation exchange capacity (CEC), exchangeable acidity and percent base saturation for the top layer (LT) and bottom layer (LB) of Ahokor clay at pH4, 5, 7, 8, and 9 are shown in Tables 1 and 2 respectively.

At the different pH values, exchangeable calcium cations ($Ca^{2+}$) were between 0.331±0.030 cmol $kg^{-1}$ and 0.920±0.025 $cmolkg^{-1}$ for the top layer (LT) while that of the bottom layer (LB) ranged between 0.331±0.030 $cmolkg^{-1}$ and 0.920 ±0.025 $cmolkg^{-1}$ for the top layer (LT). Values for the bottom layer (LB) ranged between 0.208±0.008 $cmolkg^{-1}$ and 1.959±0.020 $cmolkg^{-1}$. In both layer, the lowest and highest values of $Ca^{2+}$ were recorded at pH4 and pH9 respectively. For exchangeable magnesium cations ($Mg^{2+}$), the highest concentra- tions were obtained at the alkaline pH of 9 for both layers with values of 0.298±0.027 $cmolkg^{-1}$ and 0.358±0.036 $cmolkg^{-1}$ recorded for LT and LB respectively. The lowest concentration of $Mg^{2+}$ was observed at pH4 with values of 0.051±0.001 $cmolkg^{-1}$ and 0.035±0.003 $cmolkg^{-1}$ obtained for LT and LB respectively.

**Table 1**. Exchangeable Bases (EB), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Base Saturation (%) obtained at different pH of Ahokor Clay top Layer (**LT).**

| | $CmolKg^{-1}$ | | | | | | % |
|---|---|---|---|---|---|---|---|
| **pH** | **Ca** | **Mg** | **K** | **Na** | **CEC** | **EA** | **Base Sat.** |
| 4 | 0.331± 0.030 | 0.051±0.001 | 0.816±0.090 | 0.701±0.010 | 6.991±0.293 | 5.722±0.293 | 27 |
| 5 | 0.435±0.021 | 0.113±0.013 | 0.850±0.166 | 0.162±0.018 | 11.230±0.115 | 9.673±0.115 | 14 |
| 7 | 0.886±0.020 | 0.156±0.004 | 1.120±0.300 | 0.203±0.040 | 15.648±0.290 | 13.283±0.230 | 15 |
| 8 | 0.375±0.025 | 0.088±0.004 | 0.432±0.009 | 0.177±0.018 | 5.989±0.069 | 4.917±0.069 | 18 |
| 9 | 0.920±0.025 | 0.298±0.027 | 0.159±0.008 | 0.495±0.055 | 6.394±0.126 | 4.522±0.126 | 29 |

**Table 2**. Exchangeable Bases (EB), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Base Saturation (%) obtained at different pH of Ahokor Clay bottom Layer (**LB).**

| | $CmolKg^{-1}$ | | | | | | % |
|---|---|---|---|---|---|---|---|
| **pH** | **Ca** | **Mg** | **K** | **Na** | **CEC** | **EA** | **Base Sat.** |
| 4 | 0.208± 0.008 | 0.035±0.003 | 1.022±0.041 | 0.080±0.003 | 3.983±0.082 | 2.631±0.082 | 34 |
| 5 | 0.287±0.090 | 0.078±0.006 | 1.177±0.093 | 0.155±0.008 | 6.678±0.157 | 5.071±0.157 | 25 |
| 7 | 0.882±0.048 | 0.200±0.007 | 1.307±0.047 | 0.185±0.025 | 14.505±0.300 | 2.594±0.300 | 18 |
| 8 | 0.630±0.017 | 0.068±0.004 | 0.120±0.013 | 0.183±0.022 | 4.748±0.068 | 2.747±0.068 | 21 |
| 9 | 1.959±0.020 | 0.358±0.036 | 3.522±0.023 | 0.536±0.020 | 7.055±0.083 | 0.680±0.083 | 90 |

The values for exchangeable potassium cations ($K^+$) ranged between 0.159±0.008 $cmolkg^{-1}$ and 1.120±0.300 $cmolkg^{-1}$ for LT, while the values obtained for LB were between 0.120±0.013 $cmolkg^{-1}$ and 3.522±0.023 $cmolkg^{-1}$. For LT, the highest value for $K^+$ (1.120±0.300 $cmolkg^{-1}$) was obtained at a neutral pH (pH7). Although the highest values for $K^+$ in the bottom layer (LB) was recorded at pH9 (3.522±0.023 $cmolkg^{-1}$), the value at pH7 (1.307±0.047 $cmolkg^{-1}$) was higher than the highest value obtained for the top layer (LT) clay. Exchangeable sodium cations ($Na^+$) were between 0.162±0.018 $cmolkg^{-1}$ and 0.701±0.010 $cmolkg^{-1}$ for LT with the lowest and highest values recorded at pH5 and pH4 respectively. The $Na^+$ values for LB ranged between 0.080±0.003 $cmolkg^{-1}$ and 0.536±0.020 $cmolkg^{-1}$ with the minimum and optimum values recorded at pH4 and pH9 respectively.

Overall, there was a gradual increase in $Ca^{2+}$, $Mg^{2+}$ and $K^+$ values from the acidic medium to the neutral medium and a drop from the neutral to the alkaline medium. However, increase in pH in the acidic and alkaline media resulted in an increase in the concentrations in $Ca^{2+}$, $Mg^{2+}$ and $K^+$. The ratio of exchangeable calcium to exchangeable magnesium (Ca/Mg) provides a guide to a soil's structure which in turn influences soil drainage, root development and subsequent plant growth [29]. Well-structured soils have a Ca/Mg ratio greater than 2:1, in other words, the amount of calcium cations is more than two times greater than the amount of magnesium cations [29,30]. In the results obtained from the analysis of Ahokor clay at the various pH (Table 1 and 2), $Ca^{2+}$ was twice the amount of $Mg^{2+}$ ion. Hence, Ahokor clay may be useful in enhancing soil structure. Potassium ($K^+$), calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) are among the essential elements required by plants [31]. From the results obtained for Ahokor clay, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ are in sufficient amounts for plant uptake. Potassium ($K^+$) has substantial effect on enzyme activation, protein synthesis, photosynthesis, stomata movement and water-relation (turgor regulation and osmotic adjustment) in plants [32]. In addition, increased applications of $K^+$ have been shown to enhance photosynthetic rate, plant growth, yield and drought resistance in different crops under water stress conditions [33–36]. From our analysis, $K^+$ is the predominant exchangeable base present in Ahokor clay with both layers containing huge amount of the cations at the different pH levels screened, although the bottom layer is richer in $K^+$ ion.

Cation Exchange Capacity (CEC) is the sum total of exchangeable cations that are adsorbed and is a measure of the ability of a clay to hold cations [37]. CEC is widely used in the characterizing clay as it determines soil fertility; the higher the CEC value, the higher the fertility of the soil [38]. Thus, clay with high CEC have the ability to hold more cations making them sufficient in calcium, magnesium and other cations and therefore a higher ability to hold water (swelling property) [6]. The cation exchange capacity (CEC) for LT ranged between 5.989 ±0.069 $cmolkg^{-1}$ and 15.648± 0.290 $cmolkg^{-1}$, while the CEC values for LB were between 3.983 ±0.082 $cmolkg^{-1}$ and 14.505±0.300 $cmolkg^{-1}$. A strong relationship exist between the pH and the CEC of Ahokor clay, as the pH was seen to directly influence the CEC values of clay in both the acidic and alkaline media. In both layers, there was a steady increase in CEC values from the acidic medium (pH4) to the neutral pH (pH7) and a decline in the alkaline medium at the top layer (LT) but varied in pattern at the bottom layer. However, the CEC value at pH 9 was higher than pH8 in both layers. The CEC values followed the order pH7> pH5 > pH4 >pH9 > pH8 for LT, while that of LB was pH7> pH9 > pH5 >pH8> pH4. In both layer, the optimum CEC values was recorded at pH7, hence at pH 7, Ahokor clay holds more cations than the other respective pH screened.

Exchangeable Acidity (EA) is a measure of the acidic hydrogen and aluminum cations held on negatively charged sites of clay. For LT, the highest EA was recorded at pH 7 (13.283±0.230 $cmolkg^{-1}$) followed closely at pH 5 (9.673±0.115 $cmolkg^{-1}$) while the minimum EA value of 4.522±0.126 $cmolkg^{-1}$ was recorded at pH9. For the bottom clay (LB), the minimum and optimum EA values of 0.680±0.083 $cmolkg^{-1}$ and 5.071±0.157 $cmolkg^{-1}$ was obtained at pH9 and pH5 respectively. Ahokor clay was more saturated with the acidic cations (EA) relative to the exchangeable bases or cations. This was further evident in the percent base saturations estimated at the different pH levels for both top layer (LT) and bottom layer (LB) of the clay as displayed in Table 1 and 2 respectively. The base saturation ranged between 14% and 29% for LT, while that of LB were between 18% and 90%. The highest percent base saturation was recorded at pH9 for both layer with the respective value of 29% and 90% recorded for LT and LB.

The results obtained from the analysis of the Ahokor clay showed that pH9 is the optimum condition for application as soil blend. At this pH, the clay contains the highest concentration of base saturation and also holds sufficient amount of all exchangeable bases especially potassium ($K^+$) ion. Potassium ($K^+$) is a macronutrient required by plants thus, using Ahokor clay directly as a soil ammendment in soils showing nutrient deficiency, would provide the necessary buffer against acid generated from plant root and soil reaction processes [36].

## CONCLUSION

The nutrient level of Ahokor clay deposit located obtained in Kogi State, Nigeria for plant uptake was evaluated. The exchangeable bases (EB), cation exchange capacity (CEC), exchangeable acidity (EA) and percent base saturation at five different pH levels (4, 5, 7, 8 and 9) for the top (LT) and bottom (LB) layers of the clay were studied. Our findings showed that both layers of the clay were rich in the plant nutrient cations particularly the much needed potassium cations ($K^+$). Furthermore, pH9 was found to be the optimum condition for direct application on soil deficient in soil nutrients. In addition, Akohor clay deposit holds promise as a potential raw material in the production of NPK (Nitrogen, Phosphorus and Potassium) fertilizer due to its richness in potassium cations.

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