

Evaluation of the Influence of pH on the Release of Exchangeable Cations from a Mixed Clay Mineral Deposit for Replenishment of Soil Nutrients

Emmanuel Enoguan Ighodaro Irabor*, Linda Esanukpe, Monday Idiaghe Imafidon, Osahon Kennedy Ogbeide, Iyobosa Gift Okunzuwa, Charles Akhadelor Unuigbe, Uwaila Omoruyi

Department of Chemistry, Faculty of Physical Sciences, University of Benin, Benin City, Nigeria

*Corresponding author: emmanuel.irabor@uniben.edu

Received: 23 June 2023; Accepted: 22 July 2023; Published: 25 July 2023

Abstract

Soil nutrients consist of minerals such as Ca, Mg, K and Na ions among others which are essential to plant growth. Soils can become deficient in these nutrients on account of pollution, flooding and over cultivation. The soil condition can be ameliorated by addition of clay minerals which are rich in aforementioned cations. The mineralogy of the clay mineral was investigated using X-ray Diffractometer (XRD) and the effect of pH variation on the release of exchangeable cations of the clay mineral deposit were investigated by varying the pH of the solution in which the clay mineral was immersed whereas the amount of the cations released were determined using Atomic Absorption Spectrophotometer (AAS) and Flame Emission Spectrophotometer. Three clay minerals clinchlore, kaolinite and illite were detected. The quantity of cations released from the clay mineral varied with pH; and the pH at which the maximum quantity of the cations were released were pH4 for K⁺ ions (4.63±0.38 cmol/kg), pH7 for Ca²⁺ (12.09±0.96 cmol/kg) and Mg²⁺ (3.48±0.08 cmol/kg) ions and pH8 for Na⁺ (7.81±0.58 cmol/kg) ions respectively for site 1. This trend was observed in the three sites that were studied. This study has revealed that different pH conditions are required if this mixed clay mineral is to be employed in the remediation of nutrient deficiency in any soil in respect of a particular mineral.

Keywords: soil nutrient; clay mineral; pH; exchangeable cations

Introduction

With the ever-increasing world population which is now well over eight (8) billion humans, (Gross, 2023; Milner & Boldsen, 2023) coupled with the upsurge in the demand for land for the purposes of building shelter and other structures which are synonymous with urbanization, there is a steady decline in the availability of land for agricultural purposes (Hou *et al.*, 2023). Climate change and global warming are also factors militating against land availability for

agricultural purposes especially in developing countries (Mirón *et al.*, 2023). In Nigeria, these problems are further aggravated by the degradation of arable land due to oil spillage, uncontrolled mining activities and perennial flooding which affects many communities along the banks of Rivers Niger and Benue that supplies the bulk of the water to agrarian communities in the country (Akpokodje & Salau, 2015; Ahmadu & Egbodion, 2013; Umaru & Adedokun, 2020). The combined effects of the aforementioned factors pose serious

threat to food security as soil nutrients which supports plant life are either buried beneath pollutants rendering them unavailable or washed away by flooding. To mitigate these serious factors which are capable of causing soil infertility which would result in low or poor yield of agricultural products in the limited arable lands, different measures have to be deployed.

Several methods are available to avoid this foreseeable occurrence. One of such methods involve the amending of soils deficient in nutrients with fertilisers, animal dungs and agricultural wastes (Aghalibe *et al.*, 2017; Abdulyekeen *et al.*, 2022; Ndzeshala *et al.*, 2023). Another viable method of soil enrichment is blending of nutrient impoverished soil with clay rich in nutrient elements. Research have shown that when clay minerals are subjected to different pH treatment, different concentrations of mineral nutrients like potassium, sodium, calcium and magnesium are released (Tahir & Marschner, 2017; Irabor *et al.*, 2020; Irabor *et al.*, 2021). Soil fertility is described as the ability of soil to hold nutrients in the right proportion to assist in plant growth (Stockdale, 2002). These soil nutrients are usually cations such as potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na^+), aluminium (Al^{3+}), ammonium (NH_4^+), iron (Fe^{2+}), hydrogen (H^+), manganese (Mn^{2+}), zinc (Zn^{2+}) and copper (Cu^{2+}); with Ca, Mg and K being the most essential elements to the sustenance of plants life (Irabor *et al.*, 2020). The ability of soils to hold these cations, is proportional to the amount of clay and organic matter present.

Clay minerals such as clinocllore, kaolinite and illite (are made up of silicates); these consist of hydrous aluminosilicate complex material arranged in well-defined octahedral and tetrahedral geometrics resulting in closely packed sheets or layers. Depending on the parent rock from which the clay was formed, the surfaces of the aluminosilicate sheets may consist of either oxygen anions and or the hydroxyl ions organized to form a closely packed hexagonal network with the anionic network neutralized by exchangeable cations such as

sodium, potassium, magnesium and calcium and; organic matter (made up of organic acids) are sources of large amount of anions which provide ready sites to bind these cations through electrostatic forces (Sarkar *et al.*, 2019; Egloffstein, 2020). Therefore, the amount of cationic nutrients present in soils for plant uptake is largely influenced by the amount of negative binding sites on clay mineral and organic matter present in soils. Whereas the requirements of plants for nutrients vary widely, available scientific data strongly support the fact that the dependence of crops like cassava, yam and maize which are highly cultivated in Nigeria require different amount of nutrients such as potassium (K) for healthy growth and productivity (Ezui *et al.*, 2017; Chude *et al.*, 2011; Adiele *et al.*, 2021; Aliyu *et al.*, 2022). Furthermore, in Nigeria, the predominant soils are derived from sedimentary rocks in the forest regions (southern part of the country) with low concentration of potassium, whereas the savannah regions (mostly in the northern part of the country) contain high potassium content from igneous and metamorphic rocks (Carsky *et al.*, 2010).

Research have shown that pH influences the release of exchangeable cations from clay minerals and each clay mineral deposit differs in composition depending on the parent rock from which they were formed, the degree of weathering to which they are exposed and in situ alteration reactions caused by hydrothermal conditions and therefore clay minerals respond differently to pH treatment (Irabor *et al.*, 2020; Irabor *et al.*, 2021). The knowledge of the optimum condition of pH required to achieve different levels of release of these plant nutrients from each clay mineral deposit in order to enrich soil deficient in any of the nutrients to enhance plant growth and the resultant increase in food production becomes imperative. This study therefore, seeks to determine the optimum pH condition to affect the release of the mineral nutrients in the clay mineral deposits being studied.

Methods

Sample Area/ Sample Collection

The samples were collected in the study area at Uhonmora, Owan West Local Government Area, Edo State, Nigeria between Latitude 6°52'14" N Longitude 5°56'54" E. The sites were demarcated as described (Chimdi *et al.*, 2012) [22]. Thus, the clay deposit was sectioned into three and marked site 1 (S1), site 2 (S2) and site 3 (S3) respectively. Fifteen (15) samples were collected per site. The samples were labelled accordingly and air-dried in the laboratory.

Sample Preparation

The samples were prepared for different analysis following published procedure described by Irabor and co-workers (Irabor *et al.*, 2021). Air-dried samples were pulverized to very fine particle sizes by using a mechanically operated ceramic pestle and mortar. The pulverized samples were sieved through a 2 µm sieve to obtain a uniform size. The sieved samples were activated at 400 °C for three (3) hours in a muffle furnace. The cation exchange capacity (CEC) and the exchangeable cations or bases (EB) of the clay samples were evaluated at the selected pH of pH 4, 5, 7 and 8 respectively. The EB were Na⁺, K⁺, Mg²⁺ and Ca²⁺. Deionized water was employed for all determination unless otherwise stated.

Estimation of Cation Exchange Capacity (CEC) and Exchangeable bases (EB)

The cation exchange capacity (CEC) and the exchangeable bases (EB) of the clay samples at the different pH were estimated following published procedure of Irabor et al and Chimdi et al (Irabor *et al.*, 2021; Chimdi *et al.*, 2012). 25 g of the activated clay sample was treated with 125 mL ammonium acetate (NH₄OAc) at pH7 in a 250 mL Erlenmeyer flask and sealed with aluminum foil. The resulting clay mixture was agitated daily for 3 hours on a mechanical shaker for 3 days.

The sample was filtered under vacuum through a Whatman filter paper No. 1 on a Buchner funnel. The residue was then washed with approximately 4mL NH₄OAc. Thereafter, the filtrate was transferred into a

250 mL volumetric flask and made to mark with 1 M NH₄OAc. Exchangeable K⁺ and Na⁺ were determined from the solution using flame emission spectrophotometer (FES) Sherwood 410 model while exchangeable Mg²⁺ and Ca²⁺ were analyzed using atomic absorption spectrophotometer (AAS) Bulk Scientific 210VGP model. Triplicate determination of the assay was carried out and the standard deviations were ascertained.

To remove the excess NH₄OAc from the residue, the residual clay was treated with approximately 6 mL of 95 % ethanol. Adsorbed NH₄⁺ in the residual clay was leached out using 25 mL of 1M KCl. The washing was repeated 4 times and the leachates collected were combined in a 250 mL volumetric flask and made to mark with 1M KCl. The CEC of the clay was estimated based on the amount of ammonium nitrogen in the residual clay which was measured using a Jenway 6051 colorimeter (Irabor *et al.*, 2021; Sáez-Plaza *et al.*, 2013). Triplicate determinations were carried out and standard deviations were ascertained.

The same procedure was adopted for the evaluation of the EB and CEC of the clay samples at pH 4, 5 and 8 respectively. However, these systems were buffered with 0.1M HCl/0.1 M potassium hydrogen phthalate (KHP) buffer 4 solution, 0.1M NaOH/ 0.1M KHP buffer 5 solution and 0.025M disodium tetraborate/ 0.1M HCl buffer 8 solutions respectively (Irabor *et al.*, 2021). All chemicals used were analytical grade from Sigma Aldrich.

Exchangeable Acidity (EA) and Percent Base Saturation

The exchangeable acidity (EA) and percent base saturation of the clay samples were evaluated using expressions 1 and 2 respectively as described in literature (Irabor *et al.*, 2020; Irabor *et al.*, 2021).

$$EA = CEC + Na^+ + K^+ + Mg^{2+} + Ca^{2+} = CEC + EB \dots \dots \dots (1)$$

$$\text{Percent base saturation} = \frac{EB}{CEC} \times 100 \dots \dots \dots (2)$$

Clay Mineralogy

For the mineralogical analysis, the composite samples of the clay were pulverized to fine particles ($\leq 2\mu\text{m}$) and were subjected to X-ray diffraction using GBC Enhanced Mini Material Analyzer (EMMA) X-ray Diffractometer with Cu, $K\alpha$ radiation source. The generator operating conditions were 40KV and 5SmA. The d- values obtained were compared with the standard X-ray powder diffraction file published by the Joint Committee on the Powder Diffraction Standards (JCPDS) for the identification of the clay minerals (Irabor & Okunkpolor, 2020; JCPDS, 1980).

standard (JCPDS) as contained in the Table 1. The clay mineral clinochlore is a member of the chlorite group of minerals which is a secondary mineral found in hydrothermal alteration of intermediate aluminosilicate containing magnesium end rich member (Irabor & Okeke, 2018). Another important clay mineral found in the deposit sites was kaolinite which is a 1:1 phyllosilicate, with characteristic non-expanding, low swelling and low cation exchange capacity (Irabor & Okunkpolor, 2020; Irabor and Dibia, 2010). The clay mineral illite which is a non-expanding clay mineral which can also be formed by the hydrothermal conversion of kaolinite, has higher ability to absorb water than kaolinite (Bentabol *et al.*, 2003; Supandi *et al.*, 2019).

Result and Discussion

The results of the clay mineral deposit evaluation revealed the presence of three prominent clay minerals, clinochlore, kaolinite and illite based on the d-values obtained from X-ray diffractograms which were compared to the standard d-values obtained from X-ray powder diffraction file

Table 1: Results of the Mineralogical Assay of Uhonmora Clay Mineral Deposit

Mineral	d-values
Clinochlore $(Mg)Al(Si_3Al)O_{10}$	7.16, 3.58, 2.45
Kaolinite $Al_2Si_2O_5(OH)_4$	7.19, 3.58, 1.49
Illite $(K_{0.7}Al_{2.1}(SiAl)_4O_{10}(OH)_2$	3.35, 2.58, 4.49

Table 2: Exchangeable Bases (EB), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Base Saturation (%) at different pH of Uhonmora Clay Mineral Site 1 (S1).

pH	Cmol/Kg				CEC	EA	% Base Sat
	Ca	Mg	K	Na			
4	3.12±0.23	1.55±0.16	4.63±0.38	1.61±0.19	14.92±0.19	4.01±0.19	73.12
5	1.91±0.10	1.28±0.17	4.43±0.15	3.77±0.38	19.76±0.34	8.37±0.34	57.64
7	12.09±0.96	3.48±0.08	3.63±0.34	0.51±0.37	24.40±0.67	2.38±0.67	90.20
8	7.97±0.05	3.82±0.14	0.53±0.38	7.81±0.58	21.37±0.17	1.24±0.17	94.20

Table 3: Exchangeable Bases (EB), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Base Saturation (%) at different pH of Uhonmora Clay Mineral Site 2 (S2).

pH	Cmol/kg				CEC	EA	% Base sat.
	Ca	Mg	K	Na			
4	1.67±0.59	1.91±0.07	6.67±0.31	0.87±0.17	14.56±0.28	4.07±0.28	71.97
5	3.35±0.24	1.82±0.04	4.35±0.34	2.80±0.04	15.78±0.12	3.46±0.12	78.07
7	5.42±0.24	2.04±0.14	1.75±0.30	0.17±0.09	19.71±2.34	9.24±2.34	47.00
8	4.85±0.13	1.88±0.05	5.55±0.20	3.16±0.03	16.26±0.57	0.82±0.57	94.90

Table 4: Exchangeable Bases (EB), Cation Exchange Capacity (CEC), Exchangeable Acidity (EA) and Base Saturation (%) at different pH of Uhonmora Clay Mineral Site 3 (S3).

pH	Cmol/kg				CEC	EA	% Base Sat
	Ca	Mg	K	Na			
4	3.15±0.19	2.17±0.10	3.85±0.24	1.01±0.10	14.35±0.14	4.17±0.14	70.94
5	3.08±0.12	1.51±0.05	3.25±0.22	2.42±0.08	15.12±0.13	4.86±0.13	67.86
7	5.25±0.35	2.22±0.28	1.32±0.08	0.73±0.12	18.10±0.84	8.58±0.84	52.6
8	2.60±0.15	1.54±0.07	3.90±0.31	2.81±0.15	16.90±0.26	6.05±0.26	64.90

The results of the exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ , Na^+), cation exchange capacity (CEC), exchangeable acidity and percentage base saturation are presented in Tables 2, 3 and 4 which represents site 1 (S1), site 2 (S2) and site 3 (S3) respectively for Uhonmora clay deposit. At the different pH, the values of exchangeable calcium cations (Ca^{2+}) obtained ranged between 1.91 ± 0.10 - 12.09 ± 0.96 cmol/kg for S1, 1.67 ± 0.59 - 5.42 ± 0.24 cmol/kg for S2 and 2.60 ± 0.15 - 5.25 ± 0.35 cmol/kg for S3 respectively. Whereas the lowest values of the exchangeable calcium cation (Ca^{2+}) were observed to have been released at pH5 (S1), pH4 (S2) and pH8 (S3), the highest values at all the three sites of the exchangeable Ca^{2+} were recorded at the neutral pH of 7 (S1, 12.09 ± 0.96 ; S2, 5.42 ± 0.24 and S3, 5.25 ± 0.35 cmol/kg) respectively. For the exchangeable magnesium cation (Mg^{2+}), the lowest concentrations were at pH5 (S1), 1.28 ± 0.17 , pH5 (S2), 1.82 ± 0.04 pH5 (S3), 1.51 ± 0.05 cmol/kg respectively while the highest values were obtained at pH8 (S1), 3.82 ± 0.14 , pH7 (S2), 2.04 ± 0.14 pH7 (S3) 2.22 ± 0.28 cmol/kg respectively.

The lowest values of the exchangeable potassium cation (K^+) were pH8 (S1), 0.53 ± 0.38 , pH7 (S2), 1.75 ± 0.30 and pH7 (S3) 1.32 ± 0.08 cmol/kg respectively. On the other hand, the highest values for the exchangeable (K^+) obtained were pH4 (S1), 4.63 ± 0.38 , pH4 (S2), 6.67 ± 0.31 and pH8 (S3), 3.90 ± 0.31 cmol/kg. The exchangeable sodium cation (Na^+) had its lowest values at pH7 (S1), 0.51 ± 0.37 , pH7 (S2), 0.17 ± 0.09 and pH7 (S3), 0.73 ± 0.12 cmol/kg respectively. While the highest values were obtained at pH8 (S1), 7.81 ± 0.58 ; pH8 (S2), 3.16 ± 0.03 and pH8 (S3), 2.81 ± 0.15 cmol/kg respectively. From the results, the optimum values of exchangeable cations obtained were pH dependent. Whereas the optimum values of the exchangeable calcium ions (Ca^{2+}) were obtained at pH7 in the three sites (S1, S2 and S3) which is neutral, the least values were obtained in the acidic medium in the three sites.

The optimal values for exchangeable magnesium cations (Mg^{2+}) were obtained in the alkaline (site 1) and neutral (sites 2 and 3) media respectively. The lowest values were recorded in pH5 (acidic medium) in the three sites. The highest exchangeable

potassium ion (K^+) concentrations were obtained in the acidic medium in sites 1 and 2 and in the alkaline medium in site 3. The least values for the exchangeable K^+ were obtained in the neutral medium in S2 and S3; and the least in alkaline medium in S1 respectively. The optimum values for exchangeable sodium cations (Na^+) were obtained in the alkaline medium in the three sites (S1, S2 and S3) studied, whereas the least values were obtained in the neutral medium. These results showed that at pH 7, the Ca^{2+}/Mg^{2+} ratio in all the three sites exceeded the 2:1, similar results were also obtained in the alkaline medium in sites 1 and 2. The ratio of exchangeable calcium and exchangeable magnesium (Ca/Mg) proves a useful guide to the soil structure and any potential problems that might influence soil drainage, root development and plant growth (Chaganti *et al.*, 2021). A well-structured soil should have a Ca/Mg ratio greater than 2:1 that is the concentration of calcium ions should more than double the concentration of magnesium (Salihaj & Bani, 2018). From the results obtained in tables 2,3 and 4, it is evident that in the neutral medium this threshold ratio of Ca/Mg was exceeded and therefore, the Uhonmora clay can be classified as being well structured.

The results obtained suggest that Uhonmora clay contains large amounts of K^+ , Na^+ , Ca^{2+} and Mg^{2+} for plant uptake (Kissel *et al.*, 2009). Studies have shown that increased application of potassium enhances the rate of photosynthesis, plant growth, yield, and drought resistance in different crops under water stress conditions (Hou *et al.*, 2019; Fontana *et al.*, 2020; Wang *et al.*, 2020). The results from this study revealed Uhonmora clay showed a significantly high concentrations of exchangeable potassium ions (K^+) at the different pH screened.

The cation exchange capacity (CEC) which is the sum of all exchangeable cations that are adsorbed, and it is a measure of the ability of clay to hold cations (Irabor *et al.*, 2021). CEC is used to characterize clay properties such as fertility, swelling (ability to retain water). There is a direct correlation between high CEC value and soil fertility (Domingues *et al.*, 2020). The CEC values of

the studies sites were S1, 14.92 ± 0.19 - 24.40 - 0.67 cmol/kg; S2, 14.56 - 0.28 - 19.71 ± 2.34 cmol/kg and S3, 14.35 ± 0.14 - 18.10 ± 0.84 cmol/kg respectively. In site 1 (S1), the CEC values increased from acidic to neutral medium pH4 (14.92 ± 0.19), pH5 (19.76 ± 0.34), pH7 (24.40 ± 0.67) and pH8 (21.37 ± 0.17). In site 2 (S2), the trend was the same pH4 (14.56 ± 0.28), pH5 (15.78 ± 0.12), pH7 (19.71 ± 2.34) and pH8 (16.26 ± 0.57). Similar trend was observed in site 3 (S3) pH4 (14.35 ± 0.14), pH5 (15.12 ± 0.13), pH7 (18.10 ± 0.84) and pH8 (16.90 ± 0.26).

The three sites showed that the highest CEC values were obtained at the neutral medium, this was followed by alkaline medium, and the acidic medium yielded the least CEC values. The values obtained showed that the CEC values were pH dependent. Similarly, Laekemariam and Kibret (Laekemariam & Kibret, 2020) observed a variation in CEC values with change in pH. The results obtained showed that the clay mineral has high CEC values which implies that it shows the ability of the clay mineral to hold the exchangeable cations and support plant uptake of the desired minerals at the various pH with the highest being pH7.

The exchangeable acidity (EA) is a measure of acidic hydrogen and aluminium held on negatively charged sites of clay (Onwuka, *et al.*, 2016). In the Uhonmora clay, the value of EA obtained varied with pH in the three sites. At site S1, the values were 1.24 ± 0.17 - 8.37 ± 0.34 cmol/kg with optimum values obtained at pH5 with the minimum values obtained at pH8; S2 values ranged between 0.82 ± 0.57 - 9.24 ± 2.34 cmol/kg with the maximum value obtained at pH7 and the least value obtained at pH8; and finally, at S3, the values ranged between 4.17 ± 0.14 - 8.58 ± 0.84 cmol/kg with the optimum values obtained at pH7 while the minimum value were obtained at pH4. The Uhonmora clay was highly saturated with base cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) with values ranging from 57.64-94.20% in site S1, 47.00-94.90% in site S2 and 52-60-70.94% in site S3. The highest values of percent base saturation were recorded at pH8 in sites S1 (94.20%)

and S2(90.90%), whereas the highest value was recorded at pH 4 (70.94%) in site S3. This variation could only be linked to the nature of the clay mineral composition in the sites studied (Alshameri, *et al.*, 2019; Nadziakiewicz *et al.*, 2019).

The results obtained from the study of the Uhonmora clay mineral deposits showed that for sites S1 and S2, the alkaline medium held the highest number of bases and therefore, would be the optimum condition for the clay to be applied as soil blend whereas S3 had the highest percent base at pH4. The difference between the percent base saturation in the acidic and alkaline medium in site S3 is far smaller compared to what was observed in sites S1 and S2.

Conclusion

The mineralogical analysis of the clay revealed that the clay mineral deposit comprised of mixed clay minerals such as clinocllore, kaolinite and illite. The results obtained revealed that the clay at pH 7 released the maximum amount of calcium and magnesium ions and the ratio of calcium to magnesium ($\text{Ca}^{2+} / \text{Mg}^{2+}$) exceeded 2:1 which showed that it was well structured. The highest concentration of potassium ions (K^+) were released at pH4 in sites S1 and S2 and at pH8 in site S3. The sodium ions (Na^+) were released optimally at pH8 in all the sites. The optimum Base Saturation varied with pH in all the sites, the highest values were however obtained at pH8 in S1 and S2 and at pH4 in S3. This study has shown how selective release of the nutrient ions in the application of the clay to soils deficient in cation plant nutrients can be achieved by pH variation. This implies that before a clay mineral can be applied to any soil for remediation or supply of any particular nutrient, the knowledge of pH condition to which the clay mineral should be subjected to achieve the maximum release of the desired nutrient should be undertaken.

References

- Abdulyekeen, K.A., Giwa, S.O. and Ibrahim, A.A., (2022). Bioremediation of used motor oil-contaminated soil using animal dung as stimulants. In *Animal Manure: Agricultural and Biotechnological Applications* (pp. 185-215). Cham: Springer International Publishing.
https://doi.org/10.1007/978-3-030-97291-2_10
- Adiele, J.G., Schut, A.G., Ezui, K.S., Pypers, P. and Giller, K.E., (2021). Dynamics of NPK demand and uptake in cassava. *Agronomy for Sustainable Development*, 41, pp.1-14.
<https://doi.org/10.1007/s13593-020-00649-w>
- Aghalibe, C.U., Igwe, J.C. and Obike, A.I., (2017). Studies on the removal of petroleum hydrocarbons (PHCs) from a crude oil impacted soil amended with cow dung, poultry manure and npk fertilizer. *Chemistry Research Journal*, 2(4) 22-30. www.chemrj.org. ISSN: 2455-8990
- Ahmadu, J. and Egbodion, J., (2013). Effect of oil spillage on cassava production in Niger Delta region of Nigeria. *American Journal of Experimental Agriculture*, 3(4), 914-926.
- Akpokodje, J. and Salau, S., (2015). Oil pollution and agricultural productivity in the Niger Delta of Nigeria. *Environmental economics*, 6 (4), 68-75.
- Aliyu, K.T., Kamara, A.Y., Huising, E.J., Jibrin, J.M., Shehu, B.M., Rurinda, J., Adam, A.M., Mohammed, I.B. and Vanlauwe, B. (2022). Maize nutrient yield response and requirement in the maize belt of Nigeria. *Environmental Research Letters*, 17(6):064025.
<https://doi.org/10.1088/1748-9326/ac5bb1>

- Alshameri, A., Wei, X., Wang, H., Fuguo, Y., Chen, X., He, H., Yan, C. and Xu, F., (2019). A review of the role of natural clay minerals as effective adsorbents and an alternative source of minerals. *Minerals*, 49-64. <https://doi.org/10.5772/intechopen.87260>
- Bentabol, M., Rurz Cruz, M.D., Huetas F.J., and Linares J., (2003). Hydrothermal transformation of kaolinite to illite at 200 and 300°C. *Clay Minerals* 38(2):161-172. <https://doi.org/10.1180/0009855033820086>
- Carsky, R.J., Asiedu, R. and Cornet, D., (2010). Review of soil fertility management for yam-based systems in West Africa. *African Journal of Root and Tuber Crops*, 8(2):1-17
- Chaganti, V.N., Culman, S.W., Herms, C., Sprunger, C.D., Brock, C., Leiva Soto, A. and Doohan, D., (2021). Base cation saturation ratios, soil health, and yield in organic field crops. *Agronomy Journal*, 113(5):4190-4200. <https://doi.org/10.1002/agi2.20785>
- Chimdi, A., Gebrekidan, H., Kibret, K., and Tadesse, A., (2012). Status of selected physicochemical properties of soils under different land use systems of Western Oromia, Ethiopia. *Journal of Biodiversity and Environmental Sciences* 2(3), 57-71.
- Chude, V.O., Olayiwola S.O., Osho, A.O. and Daudu, C.K., (2011). Fertilizer use and management practices for crops in Nigeria. 4th Edition, Federal Fertilizer Department of Federal Ministry of Agriculture and Rural Development, 215.
- Domingues, R.R., Sánchez-Monedero, M.A., Spokas, K.A., Melo, L.C., Trugilho, P.F., Valenciano, M.N. and Silva, C.A., (2020). Enhancing cation exchange capacity of weathered soils using biochar: Feedstock, pyrolysis conditions and addition rate. *Agronomy*, 10(6), 824. <https://doi.org/10.3390/agronomy10060824>
- Egloffstein, T. (2020). Properties and test methods to assess bentonite used in geosynthetic clay liners. In *Geosynthetic clay liners* (pp. 51-72). CRC Press. <https://www.taylorfrancis.com/chapters/edit/10.1201/9781003077848-8>
- Ezui, K. S. Franke, A. C., Ahiabor, B. D. K., Tetteh, F. M., Sogbedji, J., Janssen, B. H., Mando A., and Giller, K. E., (2017). Understanding cassava yield response to soil and fertilizer nutrient supply in West Africa. *Plant and Soil*, 42,331-347. <https://doi.org/10.1007/s11104-017-3387-6>
- Fontana, J.E., Wang, G., Sun, R., Xue, H., Li, Q., Liu, J., Davis, K.E., Thornburg, T.E., Zhang, B., Zhang, Z. and Pan, X., (2020). Impact of potassium deficiency on cotton growth, development and potential microRNA-mediated mechanism. *Plant Physiology and Biochemistry*, 153:72-80. <https://doi.org/10.1016/j.plaphy.2020.05.006>
- Gross, M., (2023). Human population at the crossroads. *Current Biology*, 33 (1), R1-R3. <https://doi.org/10.1016/j.cub.2022.12.030>
- heterogeneity in smallholder farms of southern Ethiopia. *Applied and Environmental Soil Science*, 2020, 1-16. <https://doi.org/10.1155/2020/6161059>
- Hou, W., Tränkner, M., Lu, J., Yan, J., Huang, S., Ren, T., Cong, R. and Li, X., (2019). Interactive effects of nitrogen and potassium on photosynthesis and photosynthetic nitrogen allocation of rice leaves. *BMC plant biology*, 19(1): 1-13. <https://doi.org/10.1186/s12870-019-1894-8>

- Hou, Y., Chen, Y., Li, Z. and Wang, Y., (2023). Changes in Land Use Pattern and Structure under the Rapid Urbanization of the Tarim River Basin. *Land*, 12(3), 693. <https://doi.org/10.3390/land12030693>
- Irabor, E.E.I and Okunkpolor, A.K., (2020). Physico-chemical and mineralogical properties of a clay mineral deposit in Geheku, Kogi State, Nigeria. *Journal of Chemical Society of Nigeria* 45(4):698-704. <https://www.journals.chemsociety.org.ng/index.php/jcsn/article/view/500>
- Irabor, E.E.I. and Okeke, E., (2018). Chemical, mineralogical and engineering properties of Dangara clay mineral deposit in Kwali Area Council, Abuja, Nigeria. *The Journal of the Nigerian Institution of Production Engineers* 22,309-321.
- Irabor, E.E.I., Unuigbo, C. A., Omoruyi, U., Ehimikhuai K. O., and Sama, F. J., (2020). Evaluation of the available plant nutrients at different pH levels of Ahokor clay deposit located in Kogi State, Nigeria. *J. Chem. Soc. Nigeria*, 45 (4), 680-686. <https://www.journals.chemsociety.org.ng/index.php/jcsn/article/view/504>
- Irabor, E.E.I., Unuigbo, C. A., Udugbezi, T. D., and Omoruyi, U., (2021). Evaluation of some chemical properties of Gehuku clay deposit in Kogi State, Nigeria for possible application as soil blends. *ChemSearch Journal*, 12 (2) 23-30. <https://www.ajol.info/index.php/csj/article/view/220145>
- Irabor, E.E.I. and Dibia, E.N., (2010). The mineralogical dispersion of selected lateritic iron ore deposits at Igarrah, Edo State, Nigeria. *Journal of Science, Engineering and Technology* 17(2):9516-9525.
- J.C.P.D.S (1980). Mineral powder diffraction file vols. I & II Published by International Centre for Diffraction Data, Parkland, USA.
- Kissel, D. E., Sonon, L., Vendrell, P. F., and Isaac, R. A., (2009). Salt concentration and measurement of soil pH. *Commun. Soil Sci. Plant Anal.* 40, 179-187. <https://doi.org/10.1080/00103620802625377>
- Laekemariam, F. and Kibret, K., (2020). Explaining soil
- Milner, G.R., Boldsen, J.L., (2023). Population trends and the transition to agriculture: Global processes as seen from North America. *Proceedings of the National Academy of Sciences*, 120(4), p.e2209478119. <https://doi.org/10.1073/pnas.2209478119>
- Mirón, I. J., Linares, C. and Díaz, J., (2023). The influence of climate change on food production and food safety, *Environmental Research*, 216, 114674. <https://doi.org/10.1016/j.envres.2022.114674>
- Nadziakiewicz, M., Kehoe, S. and Micek, P., (2019). Physico-chemical properties of clay minerals and their use as a health promoting feed additive. *Animals*, 9(10):714. <https://doi.org/10.3390/ani9100714>
- Ndzheshala, S.D., Obalum, S.E. and Igwe, C.A., (2023). Some utilisation options for cattle dung as soil amendment and their effects in coarse-textured Ultisols and maize growth. *International journal of recycling organic waste in agriculture*, 12(1), 123-139.
- Onwuka, M.I., Ozurumba, U.V. and Nkwocha, O.S., (2016). Changes in soil pH and exchangeable acidity of selected parent materials as influenced by amendments in South-East of Nigeria. *Journal of Geoscience and Environment protection*, 4(5): 80-88. <https://doi.org/10.4236/gep.2016.45008>

- Sáez-Plaza, P., Navas, M.J., Wybraniec, S., Michałowski, T. and Asuero, A.G., (2013). An overview of the Kjeldahl method of nitrogen determination. Part II. Sample preparation, working scale, instrumental finish, and quality control. *Critical Reviews in Analytical Chemistry*, 43(4):224-272.
<https://doi.org/10.1080/10408347.2012.751787>
- Salihaj, M. and Bani, A., (2018). Chemical Properties of Serpentine Soils from Kosovo. *Albanian J. Agric. Sci.* 17, 78–83.
- Sarkar, B. Rusmin, R. Ugochukwu, U.C. Mukhopadhyay, R. and Manjaiah, K.M. (2019). Modified clay minerals for environmental applications. In *Modified clay and zeolite nanocomposite materials* (pp. 113-127), Elsevier.
<https://doi.org/10.1016/B978-0-12-814617-0.00003-7>
- Stockdale, E.A., Shepherd, M.A., Fortune, S. and Cuttle, S.P., (2002). Soil fertility in organic farming systems—fundamentally different? *Soil use and management*, 18,301-308.
<https://doi.org/10.1111/j.1475-2743.2002.tb00272.x>
- Supandi, S., Zakaria, Z., Sukiyah, E., and Sudradjat, A., (2019). The influence of kaolinite -illite toward mechanical properties of claystone. *Open Geosciences*, 11(1):440-446.
<https://doi.org/10.1515/geo-2019-0035>
- Tahir, S. and Marschner, P., (2017). Clay addition to sandy soil reduces nutrient leaching—effect of clay concentration and ped size. *Communications in soil science and plant analysis*, 48(15), 1813-1821.
<https://doi.org/10.30486/ijrowa.2022.1934239.1284>
- Umaru, E.T. and Adedokun, A., (2020). Geospatial analysis of flood risk and vulnerability assessment along river Benue Basin of Kogi State. *Journal of Geographic Information System*, 12(1), 1-14.
<https://doi.org/10.4236/jgis.2020.121001>
- Wang, Y., Zhang, Z., Liang, Y., Han, Y., Han, Y. and Tan, J., (2020). High potassium application rate increased grain yield of shading-stressed winter wheat by improving photosynthesis and photosynthate translocation. *Frontiers in Plant Science*, 11: 1-10.
<https://doi.org/10.3389/fpls.2020.00134>