

SURFACE CHARGE CHARACTERISTICS OF SOME BASALTIC SOILS IN CROSS RIVER STATE, NIGERIA



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ABSTRACT

Physicochemical and mineralogical properties, iron and aluminium oxides as well as Point of Zero Charge (PZC) of basaltic soils of Cross River State, Nigeria were studied. Four profiles with two each representing soils from Obubra and Ikom LGA respectively were studied. The soils are deep (>100cm) and well-drained. They are coarse-textured with a high sand content exceeding 70% in the surface, giving surface textural classes of loamy sand or sandy loam overlying sandy clay and sandy clay loam subsurface. Clay content of 20% in the subsurface of the soils can retain considerable amount of water for crop production. The soils are characterized as follows: soil reaction, strongly to moderately acidic (pH 5.3-5.7, organic carbon mean value of 1.93 % for surface soil; available phosphorous (P) (10.46 mgkg⁻¹); Effective Cation Exchange Capacity (ECEC) is moderate (4.76-12.13comlkg⁻¹); base saturation (89.1-93.5%). Others were mean total free Fe₂O₃ (0.97-1.03%); total free Al₂O₃ (0.06-0.11%); amorphous Fe₂O₃ (0.30- 0.30 %); organically-bound iron (0.07-0.20%); the mean active iron ratios were 0.30 and 0.54. The minerals in the clay fraction were as follows: Quartz (30.9-42.35%) and kaolinite (57.7-68.9%). Point of Zero Charge (PZC) values were 4.7 and 5 in Ikom and Obubra respectively, indicating the PZC values of typical natural soils. The findings reveal that the surface charge depends on activities of potential determining ions (H⁺ and OH⁻) and electrolyte concentration (ionic strength, I), sesquioxides and amorphous colloids. With the negative delta pH (Δ pH) values in all the horizons, the basaltic soils are negatively charged and may not have capacity to attract negative anions (NO³⁻; Cl⁻) which are also negatively charged.

INTRODUCTION

Surface charge characteristics are based on the charge properties of soil constituents/components such as kaolinite, sesquioxides and organic matter. kaolinite and organic matter can generate negative charges, while the sesquioxides (gibbsite, goethite and hematite) can bear positive charges (Shamshuddin and Anda, 2008). Based on differences in surface characteristics, soils can be categorized as permanent charge and variable-charge soils. The permanent charge soils (constant surface charge type) are soils of the temperate region, where the charges arise from Isomorphous substitution in the 2:1 clays, whereas, the variable-charge soils (constant potential type) where the charges arise from ionization of hydroxyls of the 1:1 clays and hydrous oxides (Loganathan and Fernando, 1977; Moghimi *et al.*, 2013) in tropical soils. Depending on soil pH, the variable charge surfaces can generate net negative, positive or no charge. The pH at which the net electric charge is zero is called the Point of Zero Charge, which is one of the most important parameters used to describe variable-charge surface (Appel *et al.*, 2003).

Surface charge of soil colloids is responsible for various important physicochemical properties such as ion exchange, ion mobility, aggregate stability, erosivity among others (Loganathan and Fenando, 1977). Surface charge characteristics for colloids can predict the mechanisms of reactions with xenobiotic compounds and pathways of weathering reactions in soils (Schroth and Sposito, 1997); Shamshuddin and Anda, 2008). Surface charge characteristics for colloids with amphoteric surfaces influence soil management in agriculture and retention of ionic soil contaminants (Appel *et al.*, 2003). Surface charge characteristics control migration of ions in

soils, the formation of organomineral complexes, soils structure, plant nutrition and the dispersion, flocculation, swelling and shrinkage of the soil fractions (Moghimy *et al.*, 2013).

The point of zero charge is the pH at which the net electric charge is zero and it is one of the most important parameters used to describe variable - charge surface (Appel *et al.*, 2003). Several studies have reported PZC values of 3.9 – 4.3 for subsoils, (30 – 60cm) of Ultisols from Ocone county (USA) and Sumatra (Indonesia), as well as 4.4 – 4.5 for the oxisols from Queensland (Australia) (Qafoku *et al.*, 2000); others obtained the PZC values of 4.2 and 3.7 for oxisols and Ultisols, respectively from Puerto Rico (Appel *et al.*, 2003) while Gallez *et al.*, 1976 reported values of 4.0 and 5.5 for subsoil Ultisols and oxisols, respectively in Nigeria.

Soils in Ikom and Iyamayong-Obubra (Basalt) are highly weathered and classified as *Ultisols*. Being in humid tropical environment, the soils may be characterized as constant surface potential materials whose potential determining ions (H⁺ and OH⁻) control the surface charge characteristics of the soil. The objectives of this study were to determine the physicochemical and mineralogical properties, iron and aluminium oxides as well as point of zero charge of basaltic soils of Cross River State, Nigeria.

MATERIALS AND METHODS

Four profile pits were dug and sixteen soil samples were collected from these profiles in the two locations namely; Ikom, and Obubra Local Government Areas. Basaltic soils of Ikom (05^o 58' 59'' N, 008^o 21' 42'' E) and Obubra (05^o 56' 72'' N, 008^o 42' 16'' E) were used for the study with coordinates obtained using Garmin etrex (2000) GPS meter. Their mean annual rainfall ranges from 2290 - 2680 mm per annum with distinct dry season of four months between November and March, mean daily temperature varies from 24 - 32 °C and mean relative humidity varies from 82 - 87 % (Akpan-Idiok, 2012)

The particle size distributions of the soil were carried out using Bouyoucos hydrometer method, Soil pH was determined potentiometrically using glass electrode. Total nitrogen was determined using macro-Kjeldhal method. Available phosphorus was determined using Bray 1 method, Exchangeable bases: Ca, Mg, K and Na was extracted with 1N NH₄OAC at pH 7. Ca and Mg were determined by the EDTA, while K and Na were determined by flame photometric method, Exchangeable acidity were extracted with 1M KCl solution and the acidity from the extracts will be ensured by titrated with 0.01M NaOH. Effective cation exchange determination was obtained by the summation of exchangeable cations and acidity. Organic carbon was determined by Walkley and Black method all as described by Udo *et al.* (2009).

Percentage base saturation was calculated using the formula below:

$$\% \text{ B.S} = \frac{\text{Total Exchangeable Bases} \times 100}{\text{ECEC}}$$

Determination of iron and aluminium oxides

Total iron and aluminium oxides were extracted by hydrofluoric/perchloric acid digestion. Free iron and aluminium oxides were extracted by Dithionite-Citrate-Bicarbonate (DCB) (Mehra and Jackson, 1960). Amorphous iron and aluminium oxides were extracted by acidified ammonium oxalate (McKeage and Day, 1966). Iron and aluminium concentrations in all the extracts were determined using atomic absorption spectrophotometry (Naidu *et al.*, 1997)

Determination of clay minerals in the soils

The X-Ray Diffraction (XRD) pattern of clay mineral was recorded with a Philips Diffractometer, using Co K α radiation in order to allow for a more reliable comparison between the relative heights of peaks in the XRD data as outlined by (Duane and Robert 1997).

Determination of point of zero charge

This was carried out as outlined by (Longanathan and Fernando, 1977).

RESULTS AND DISCUSSION

Physical properties - particle size distribution

The sand fraction mean values was 54.0 % in the subsurface of Basaltic soils (Table I).The silt fraction mean values was 8.0 % in the surface basaltic soils; clay fraction mean was 38.0% in subsurface of basaltic soils. The basaltic soils are coarse-textured with a high content of sand exceeding 70% in the surface, giving surface textural classes of loamy sand or sandy loam in basaltic soil (Table 1). Basaltic soil can retain considerable amount of water for crop production. Similar results were obtained for basaltic soils of Cross River State, Nigeria. (Akpan-Idiok *et al*, 2004 and Akpan-Idiok, 2012)

Chemical Properties

The chemical characteristic data are shown in Table 2a & b. The pH values (5.3-5.7) classify for basaltic soils as strongly to moderately acidic with mean values of 5.4 and 5.7 in surface and subsurface soils, respectively. The findings are consistent with the results of the earlier workers on basaltic soil (Eshett, 1987; Akpan *et al*, 2004; Akpan-Idiok, 2012).

Table 1: Range, Mean and Standard error for some physical properties

Parameters	Basaltic soils			
	Surface		Subsurface	
	Range	Mean	Range	Mean
Sand (%)	69.0-78	73±1.96	44-65	54±1.94
Silt (%)	12-19	16.5±1.55	3-14	8.0±1.03
Clay (%)	9-12	10.5±0.65	22-51	38.0±2.66
Texture	-	Sandy loam	-	Sandy clay

Table 2: Range, Mean and Standard errors for some physio-chemical properties

Parameters	Basaltic soils			
	Surface		Subsurface	
	Range	Mean	Range	Mean
pH	5.3-5.7	5.43±0.09	5.2-6.0	5.68±0.08
Organic Carbon (%)	1.08-2.53	1.93±0.35	0.24-1.18	0.54±0.09
Total Nitrogen (%)	0.09-0.21	0.17±0.03	0.01-0.10	0.04±0.01
Available P (mg/g)	1.04-23.87	10.54±5.1	0.55-27.35	9.88±2.48
Calcium(cmol/kg)	4.8-7.4	6.25±0.54	1.8-6.2	2.7±0.40
Mg ²⁺ (cmol/kg)	2.2-4.2	3.3±0.48	0.8-4.6	2.65±0.41
K ⁺ (cmol/kg)	0.09-0.12	0.12±3.0x10 ⁻³	0.09-0.13	0.11±3.75x10 ⁻³
Na ²⁺ (cmol/kg)	0.08-0.09	0.09±2.89x10 ⁻³	0.07-0.10	0.08±2.89x10 ⁻³
ECEC (cmol/kg)	7.99-12.13	10.40±0.9	4.76-11.65	7.90±0.67
Exchangeable acidity(cmol/kg)	0.48-0.88	0.66±0.33	0.28-1.40	0.65±0.02
Base saturation (%)	90-96	93.5±1.26	75-96	89.1±1.90
ΔpH	-0.6-(1.6)	-1.08	-0.8-(-2.3)	-5.52

Organic carbon contents had surface mean value of 1.93 % (Table 2a).This level of organic carbon is rated medium as most values are greater than 1.5% (Enwezor *et al.*, 1989). Total nitrogen contents were low (0.01-0.23%) (Table 2a) as most values were below 0.2% (Metson, 1961) established for productive soils. This low content of total nitrogen could be ascribed to rapid microbial activities, leaching of nitrates and crop removal in the soil environment. Similar ranges of values (0.08-0.20 %) were reported for basaltic soils in Cross River State of Nigeria (Akpan-Idiok *et al*, 2004; Akpan-Idiok and Ukwang, 2012). Available P means values was 10.54mgkg⁻¹ (Table 2a). The basaltic soils are rated low in P content; this could be ascribed to strong acidic conditions, presence of sesquioxides and soil parent materials with poor phosphorus minerals/contents (Eshett, 1987; Akpan-Idiok *et al*, 2004).

The exchangeable bases mean values for surface and subsurface plain soils were as follows: Ca (6.25 and 2.7cmolkg⁻¹) Mg (3.3 and 2.65cmolkg⁻¹); K(0.12 and 0.11 cmolkg⁻¹) and Na(0.09 and

0.08 cmolkg⁻¹) as shown in Table 2. These values are low when compared with the medium range critical values of individual basic cations: 5-10, 1-3, 0.3-0.6 and 0.3-0.7cmolkg⁻¹ (Holland *et al*, 1989) for crop production in the ecological zone. Exchangeable acidity values were low (mean, 0.25 - 0.66) for basaltic soils (Table 2) when compared with a medium range of 2.1-4 cmolkg⁻¹ (Holland *et al.*, 1989). However, impact of Al³⁺ in the soil solution could be significant in terms of influencing the biochemical behaviour in the soils (Akpan-Idiok, 2012). Effective Cation Exchange Capacity (ECEC) values for basaltic soils (4.76-12.13 cmolkg⁻¹) were rated medium when compared with the threshold value of 10 cmolkg⁻¹ (FPDD, 1990) established for productive soils (Table 2). The high rainfall (mean annual, 2290-2680 mm) for basaltic soils might have enhanced the leaching of basic cations from the soil solum (Akpan-Idiok *et al*, 2004; Akpan-Idiok, 2012). With mean percentage Base saturation of 93.5 and 89.1 for surface and subsurface respectively (Table 2), basic nutrients occur in available forms in soil solution despite the low cation reserves in the soils.

Extractable Iron and Aluminium Oxides

Total free iron and aluminium oxides refer to forms removed by Dithionite-Citrate- Bicarbonate (DCB) method (Ball and Beaumont, 1972). Total free iron mean values were 1.03 and 0.97% in surface and subsurface of basaltic soils (Table 3). The amount of free iron was high in basaltic soils. This amount may reflect the red colour of the soils observed in the field during sampling.

Amorphous Iron and Aluminium (Oxalate Extractable) Oxide

Amorphous iron and aluminium oxides constitute “aged” hydrous oxides solubilized by acid ammonium oxalate (Ball and Beaumont, 1972; Akpan-Idiok, 2002). The amorphous iron mean values were 0.30 % in both surface and subsurface soils respectively (Table 3), though, the amounts of amorphous iron for basaltic were lesser. Similar results were obtained by Akpan-Idiok and Opuwaribo (1992) for soils in Rivers State of Nigeria.

Organically-Bound Iron and Aluminium (Pyrophosphate extractable) oxides (Pr-Fe₂O₃, Pr-Al₂O₃).

The organically-bound iron (Pr-Fe₂O₃) consists of amorphous “fresh” hydrous oxides removed by alkali pyrophosphate (Aghimien *et al*, 1998, Akpan-Idiok, 2002). The organically-bound iron mean values were 0.19 % and 0.07 % in surface and subsurface respectively for basaltic soils, (Table 3).

Table3: Range, mean and standard Errors for different forms of iron oxides.

Parameters	Basaltic soils			
	Surface		Subsurface	
	Range	Mean	Range	Mean
DBC(d-Fe ₂ O ₃)%	0.85-1.21	1.03±0.08	0.08-1.53	0.97±0.12
(Ox-Fe ₂ O ₃)%	0.29-0.31	0.30±3.9 X10 ⁻³	0.27-0.36	0.30 ± 0.66
(Pr-Fe ₂ O ₃) %	0.12-0.25	0.19± 0.03	0.01-0.33	0.07 ± 0.03
(O/d) (mg/kg)	0.24-0.45	0.29 ± 0.02	0.24-3.3	0.54 ± 0.25
(Pr/d) (mg/kg)	0.14-0.24	0.29 ± 0.03	0.11-0.27	0.08 ± 0.03

Table 4: Range, Mean and Standard errors for different forms of aluminium oxides

Soil parameter	Basaltic soils			
	Surface		Subsurface	
	Range	Mean	Range	Mean
(d-Al ₂ O ₃)%	0.01-0.09	0.06+0.02	0.00-0.32	0.11+0.03
(Ox-Al ₂ O ₃) %	0.08-0.86	0.53+0.17	0.82-0.75	0.56+0.06
(Pr- Al ₂ O ₃) %	0.16-0.37	0.29+0.05	0.07-0.31	0.16+0.02
(Ox/d) (mg/kg)	540-2110	10.82±3.51	8.7-41.0	9.51+3.17
(Pr/d) (mg/kg)	1.70-38.33	13.32+8.51	0.35-8.44	2.67+0.77

The amounts of organically-bound iron (mean, 0.07 %) is greater than that of the total free iron oxides (means, 0.51 %). The accumulation of organically bound aluminium (mean, 0.29 %) is

relatively higher than the total free aluminium oxides (mean, 0.06 %) for the basaltic soils (Table 4). Although dithionite citrate-bicarbonate method should remove crystalline, amorphous “aged” and “fresh” hydrous oxides with higher values than the pyrophosphate-extractable Al_2O_3 , data obtained for the soils in Table 4 contradict this view. Pyrophosphate extractable Al_2O_3 , values have been found to be higher than dithionite extractable Al_2O_3 .

This is an anomaly but the explanation to the phenomenon is that pyrophosphate extractant may dissolve some other compounds of aluminium particularly destroying the clay minerals and thus releasing the aluminium content of the clay minerals. This probably accounts for the high contents of Al_2O_3 , in pyrophosphate extracts. Similar results were obtained by Aghimien *et al.*, (1998) for the hydromorphic soils of Southern Nigeria and by Akpan-Idiok and Opuwaribo (1992) for some soils in Rivers State of Nigeria.

Iron and Aluminium Ratios

The “active” iron or aluminum ratio is an indication of the relative amounts of amorphous and free iron or aluminium in soils (Blume and Schwartzman, 1969); Akpan-Idiok and Opuwaribo (1997). The amorphous is more reactive and more important in soils processes than the free form (Mitchell *et al.*, 1964). According to Aghimien *et al.*, (1998) a high active ratio indicates a relatively high content of the amorphous form and a high reactivity of the free oxides in the soils. The mean active iron ratios were 0.29 for surface of basaltic soil (Table 3). Similarly, the mean active aluminum ratios were 10.82 and 9.51 for surface and subsurface soils, respectively. In well-drained Nigerian soils Udo (1980) obtained active iron ratios of 0.03 to 0.13 in the soils, the high aluminium ratios reflect a slow rate of crystallization of aluminium oxides and a preponderance of amorphous aluminium (Akpan-Idiok and Opuwaribo (1992).

The high active iron or aluminium ratio exceeds 0.35, indicating that the soils have problems of poor drainage in the rainy season (Stonehouse and Anaud, 1971). Again, the high iron or aluminium ratio indicate large existence of free or aluminium oxide in non-crystalline form which constitutes amorphous colloids that control the surface charge in terms of generating amphoteric surfaces in soils.

MINERALOGICAL COMPOSITION

Quartz

Quartz is one of the common minerals that occur in highly weathered soils of humid tropical regions. It is an intrinsic part of sand sized grains and can persist in soil because it is chemically inert (Akpan-Idiok and Ukwang, 2012; Akpan-Idiok *et al.*, 2013). The X-ray diffraction analysis shows that quartz accounts for mean values of 47.4% and 30.9% in surface and subsurface of basaltic soils respectively (Table 5). The mineralogy of soils of southeastern Nigeria has been inherited from the parent material (Jungerius and Levelt, 1964; Chikezie *et al.*, 2010). The presence of the resistant mineral like quartz in clay fraction indicates that the soils have reached advanced stage of weathering as confirmed from the absence of weatherable minerals such as feldspars (Akpan-Idiok and Ukwang, 2012).

They also reported that chemically, quartz mineral can hardly contribute to soil fertility or plant nutrition. However, its interaction with other soil elements improves structural stability, water permeability, biomass productivity, resistance to erosion, and aeration among others. The X-ray diffractograms of the minerals are shown in Figures 1(a-d).

Table 5: Mineralogical composition of clay fraction in basaltic soils in Cross River State, Nigeria.

Parent material		Clay minerals(%)		
		Quartz	Kaolinite	Total (%)
Basalt	Surface	42.3	57.7	100
	Subsurface	31.1	68.9	100

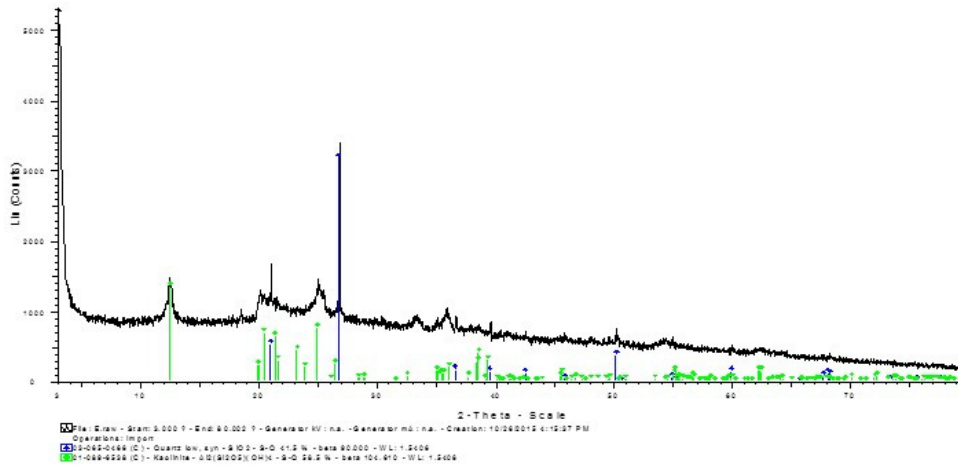


Figure 1a: XRD for surface soil of Obubra

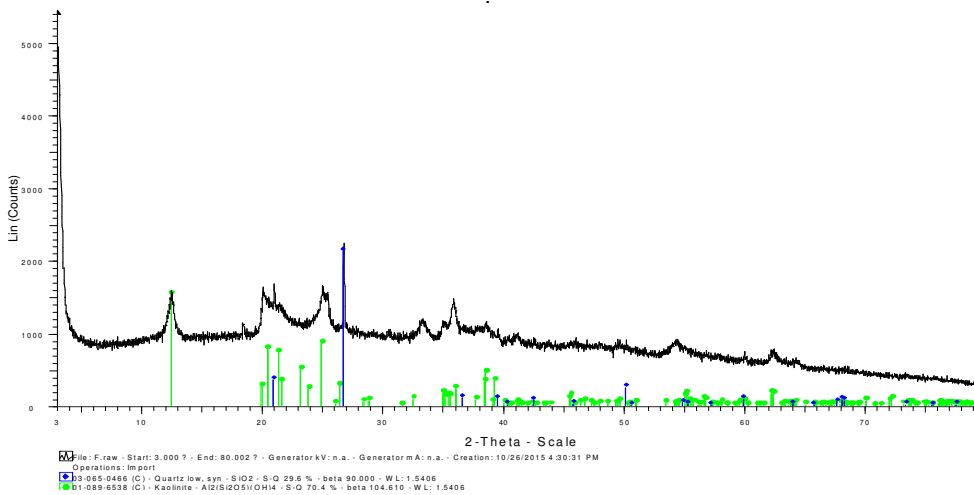


Figure 1b: XRD for subsurface soil of Obubra

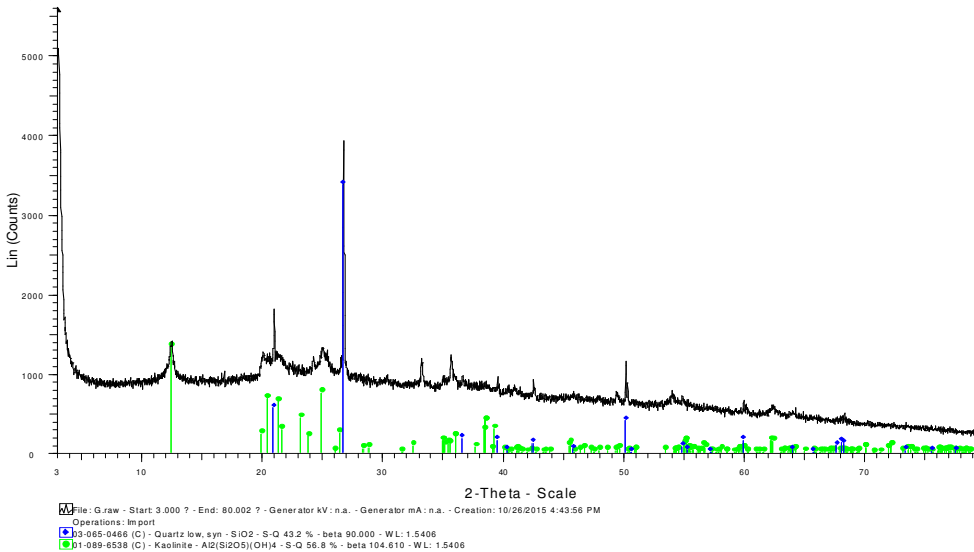


Figure 1c: XRD for surface soil of Ikom

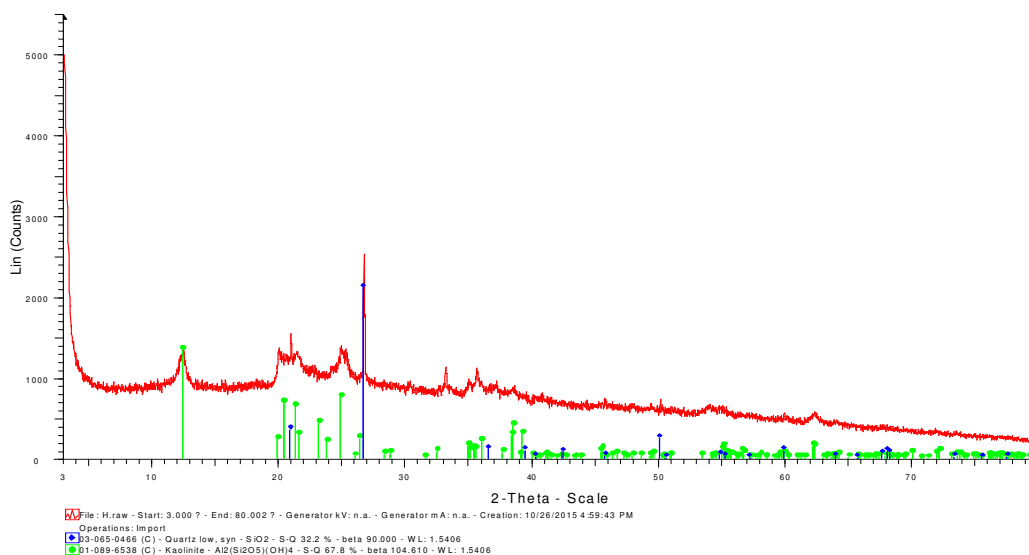


Figure 1d: XRD for subsurface soil of Ikom

Kaolinite and quartz:

Kaolinite is another most abundant clay mineral in the clay fraction of basaltic soils. The X-ray diffraction data show that kaolinite constitutes about 57.7 and 68.9% in surface and subsurface of basaltic soils respectively. The findings are consistent with the earlier studies that reported quartz and Kaolinite as dominant mineral in the clay fraction of basaltic soils. (Udo, 1977; Eshett, 1987; Akpan-Idiok and Ukwang, 2012). The implications of the identified minerals, (quartz and kaolinite) suggest that the soils have undergone advanced stage of weathering with low activity clay, low charged surface area, low cation reserve and low fertility status (Akpan-Idiok and Ukwang, 2012). Figures 1-2 present the X-ray diffractograms of the minerals.

SURFACE CHARGE CHARACTERISTICS

Delta pH values:

The difference between values of soil pH determined in INKCl solution and in distilled water.

$$\text{pH (KCl)} - \text{pH (H}_2\text{O)} = \Delta\text{pH}$$

This is referred to as delta pH (ΔpH) and it illustrates that all the horizons of the soils possess net surface negative charge. The pH in water was higher than delta pH (ΔpH) in IN KCl solution (Table 2). For basaltic soils, the delta pH (ΔpH) varied from -0.6 to -2.3 with means of -1.08 and -1.32 in surface and subsurface respectively. The soils with net negative charge can retain basic cations and heavy metal pollutants. The drop in pH in the KCl solution arises from the hydrolysis of Al^{3+} displaced by the K (Mekaru and Uehara, 1972) and being strongly acidic soils, the dominant cation on the exchange complex might be exchangeable Al^{3+} (Esu *et al*, 2008; Aki *et al*, 2014).

Point of zero charge of the soil:

The potentiometric titration curves at different ionic strength (0.001M, 0.01M, 0.1M and 1.0M) for surface of basaltic soils are shown in Figures 2 and 3. The titration curves at varying ionic strength (I) tend to intersect one another at single point when pH is plotted against surface charge or amounts of acid or base added. The point of intersection is referred to as the point of zero charge (PZC) where the net total particle charge is zero. It is the pH where the net adsorption of

potential-determining ions, H^+ and OH^- on variable-charge surfaces is independent of electrolyte concentration. In this study, the points of zero charge values of 4.8 and 5.0 were obtained for basaltic surface soils.

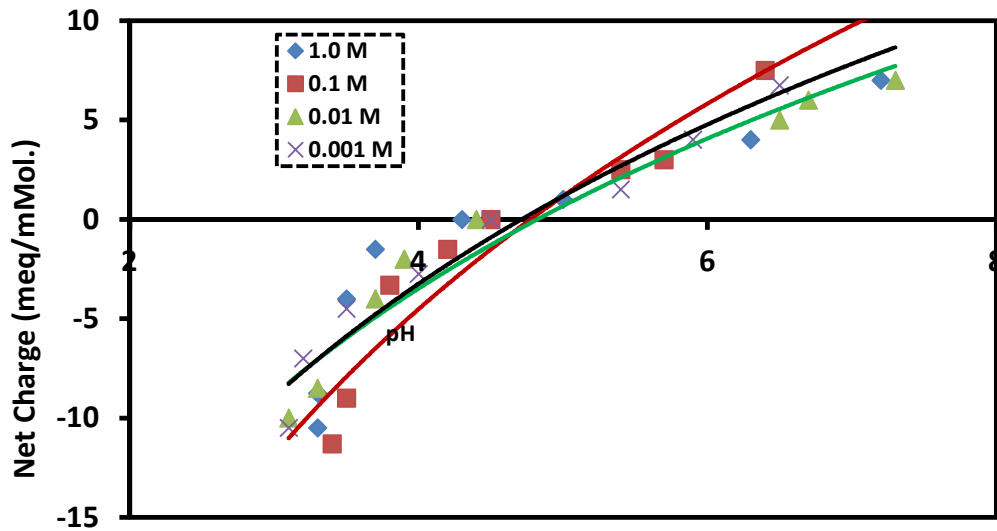


Figure 2: Surface point of zero charge for Obubra soil

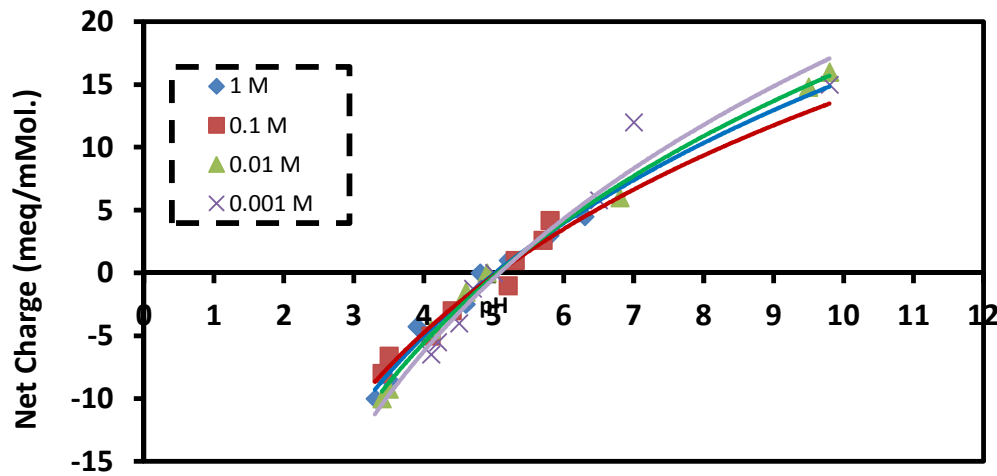


Figure 3: Surface point of zero charge for Ikom soil

The range of values is typical of natural surface soils with organic matter or iron/aluminium in the soils (Shamshuddin and Anda, 2008). Studies have shown that organic matter in the surface soils tends to lower the PZC when compared with the subsoil horizons within a given profile. Quartz and Kaolinite has PZC values below pH 3.0 whereas pure Fe and Al oxides and hydrous oxides such as hematite, goethite and gibbsite have PZC between pH 7 and 8 (Juo, 1978). For this study the surface basaltic soils of Ikom dominated by quartz and Kaolinite have PZC of 5.0 with high magnitude of electrolyte with pH-dependent charge surface. This is an indication that the soils are rich in iron oxides and have considerable variable charge. Similar results were

reported by Juo (1978) for Basaltic soils of Ikom as well as Kaolintic soils of Nkpologu, in Nigeria.

CONCLUSION

The Point of Zero Charge (PZC) refers to the pH at which the net charge is zero and is expressed as pH_0 . The PZC value is useful in predicting the nature of the surface charge or the extent of a given soil to adsorb anions (NO_3 , Cl) or cations (Ca, Mg, K). For basaltic soils, the pH_0 values are 4.8 and 5.0 while the field soil pH stands at 5.4 and 5.7. With field pH higher than the pH_0 (4.8,5.0) the basaltic soils therefore possess considerable negative charges and may have little or no capacity to retain anions such as NO_3 and Cl which are negatively charged (Juo, 1978). The delta pH (ΔpH) values classify all the horizons as negatively charged. With pH_0 values of 4.8 and 5.0 for basaltic soils, it can be inferred that the soils under study have achieved a more advanced chemical stage of weathering (Shamshuddin and Anda, 2008).

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