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Multisolvent Determination of pH of Soils from Bituminous Sands Deposit Areas of Nigeria

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Abstract: Multisolvent determination of the pH of soils from areas of Nigeria bituminous sand deposits was carried out using the electrometric method to establish the pH of the soils before the commencement of the exploitation of the bituminous sands and also to know the variation of pH of the soils using variable solvents over a range of soil to solvent dilution ratios. Soil sampling was done at two different depths viz., 0-50 cm and 50-100 cm and the samples were prepared for pH measurements using three commonly recommended solvents viz: distilled water, 0.01 M and 1 M KCl solutions. The results indicate the soil types are acid soils. This research will also add to the existing exploration data on the study area before the commencement of the exploitation of the natural resources.

Key words: pH, multisolvent, soil, bituminous sand

INTRODUCTION

Bituminous sands, otherwise known as tar sands or oil sands deposits occur in Nigeria mainly along the upper fringe of the agricultural belt which also falls in the same ecologically sensitive mangrove region of the Niger Delta of Nigeria where mining of conventional oil is currently going on[1,2]. The Nigerian bituminous sands deposit is estimated to be one of the largest deposits in the world[3] with a belt of about 120 km by 6 km. It extends from the Okiti pupa ridge/western feather edge of tertiary Niger Delta to as far west of Ijebu-Ode in Ogun state of Nigeria with an estimated reserve of about 40 billion barrels of oil sands[1,3-5]. At present, there is little or no pollution of the environment of the area because the inhabitants are primarily peasant farmers. But as exploitation of the tar sands commence, pollution would likely set in thereby altering the physico-chemical properties of the host agricultural soils. This may alter the population diversities of microbes, plants and animals of the area[6].

Soil pH as an edaphic factor is the most important chemical characteristic of soil as a medium for plant growth. It is the soil parameter used in estimating the lime requirement of soils. The activities of soil mineral ions utilized for plant nutrition depend highly on hydrogen ion concentration of the soils[6,7]. pH therefore influences the soil fertility. Likewise, predominance of cations such as Ca, Mg, Na and K tend to increase the pH of soil when released from clay.

$$\text{Clay} - \text{Na} + \text{H}_2\text{0} \rightleftarrows \text{Clay} - \text{H} + \text{Na}^+ + \text{0H}^-$$

However, cations such as Al, Fe or H^+ are desorbed from clay results in acid soil solutions due to hydrolysis of the cations.

$$\text{Clay} - \text{Al} + 5\text{H}_2\text{0} \rightleftarrows \text{Clay} - \text{H}_3 + \text{Al (0H)}_4^- + \text{H}_3\text{0}^{+[8]}.$$

Soils are usually grouped into acidity or alkalinity classes[9] this classification by far helps in indicating acid-base conditions in soils. Humid region soils are usually acid soils (pH<7.00) because frequent leaching tends to produce protonated clay which reduces the pH.

$$\text{Clay} - \text{H} + \text{H}_2\text{0} \rightleftarrows \text{Clay}^- + \text{H}_3\text{0}^+$$

On the other hand, arid soils are associated with high pH where Ca, Mg, Na and K salts accumulate.

$$\text{Clay} - \text{Ca} + \text{H}_2\text{0} \rightleftarrows \text{Clay} - \text{H} + \text{Ca}^{2+} + \text{0H}^-$$

Soil pH can be increased by liming.

$$\text{Clay} - \text{H}_2 + \text{CaC0}_3 \rightleftarrows \text{Clay} - \text{Ca} + \text{H}_2\text{0} + \text{C0}_2$$

The Clay-Ca species will increase the soil pH. Like wise soil pH is decreased by addition of acid salts such as $(NH_4)_2SO_4$ or sulphur, which will be oxidized by soil microbe (bacteria) to $H_2\,SO_4$[8].

$$2\text{S} + 3\text{0}_2 + 2\text{H}_2\text{0} \xrightarrow{\text{Bacteria}} 4\text{H}^+ + \text{S0}_4^{2-}$$
$$\text{Clay}^- + \text{H}^+ \rightleftarrows \text{Clay} - \text{H}$$

Most plants thrive well in soils with a slightly acid medium, since nearly all plant nutrients are available in

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optimal amounts at that medium, where as, soils having pH<6.0 will more likely fall short of some of the available nutrients (e.g. Ca, Mg and K) for optimal plant growth. In strongly and very strongly acid soils plants nutrients (e.g. Fe, Al and Mn) may be present in toxic amounts because of their high solubility in such media. Arid and semi-arid regions are predominantly alkaline soil (pH>7.00); the soils definitely contain low quantities of soluble Al, Fe and Mn due to the formation and subsequent precipitation of insoluble Al, Fe and Mn hydroxides. The minerals are therefore usually unavailable or available in quantities insufficient for plant development at this pH range[9].

Results of soil pH measurement vary widely with preparation procedure of the soil sample. Therefore the details of the preparation method must be stated with any soil pH data. The three commonly recommended solvents used in soil preparation for pH measurement are distilled water, 1 M KCl and 0.01 M $CaCl_2$ solutions[7,10]. The pH values in 1 M KCl solution have the advantage of being less influenced by fluctuation in biological and meteorological conditions. They show a more natural pH characteristic of the soil than in water. However the pH of soils in 0.01 M $CaCl_2$ is not much dependent of dilution over a wide range of soil -to- solvent ratios[7].

In the present study, electrometric method was used to determine the pH of soils of bituminous sands occurrence area of Nigeria using the three commonly recommended solvents viz., 1 M KCl, 0.01 M $CaCl_2$ and distilled water. In this method, the potential of a hydrogen-ion-indicating electrode is determined potentiometrically against some reference electrode which is usually a saturated calomel electrode and which also serves as a salt bridge in forming a liquid junction between the saturated KCl and the test solution[7].

MATERIALS AND METHODS

The soil samples were collected along a transverse line (1 km by length) that cuts across Foriku-Agbabu road in the bituminous sands occurrence area. Sampling was done at 100 m from both sides of the road. At each sample point, two soil samples at depths (0-50 and 50-100 cm) were collected from five points along this transverse line using a Dutch Hand Auger. This was done after all the decomposing plant materials had been removed[10]. Geographical Positioning System (GPS) was used to locate these points; while the samples were conveyed immediately to laboratory for analysis. The composites and representative soil samples were prepared by air drying at room temperature in the laboratory but properly covered to prevent air particulate contamination. These were then crushed to 2 mm mesh size using agate mortar, after homogenizing by coning and quartering[11,12].

Three alternative procedures, (Soil /water, Soil/0.01 M $CaCl_2$ and Soil/1 M KCl) involving more concentrated, dilute and more dilute suspensions (ratio of soil to solvent in order of 1:1, 1:25, 1:5 and 1:10) were used in the determination of the soil samples before pH measurement. Each test solution (soil suspension) was thoroughly stirred on magnetic stirrer for 30 min before pH measurement. The pH of the soil samples at 25°C were measured by electrometric method using a digital glass electrode pH meter model HI 8519 (Hanna Instrument).

The accuracy of the experimental values was ensured by calibrating the Glass electrode pH meter model HI8519 (Hanna Instrument) used with standard pH 4.00 buffer (0.05 M potassium biphthalate, $KHC8H_4O_4$) and pH 10.00 (carbonate) buffer respectively. The buffers were equally confirmed with Hand set glass electrode pH meter model CD70 (WPA Instrument). All the reagents used were BDH Analar Grade.

RESULTS AND DISCUSSION

The results at the two depths (0-50 and 50-100 cm) show that the pH of the soil samples increases with increasing dilution for all the soil suspensions (Table 1). For the same soil/solvents ratio, pH of soil suspensions increases in order of water > 1 M KCl > 0.01 M $CaCl_2$

Table 1: Average pH results for the soil samples at 25°C

	Soil/Water suspension ratio				Soil/0.01 M $CaCl_2$ suspension ratio				Soil/l M KCl suspension ratio			
0-50 (cm) Depth	1:1	1:2.5	1:5	1:10	1:1	1:2.5	1:5	1:10	1:1	1:2.5	1:5	1:10
Mean	4.68±0.25	4.80±0.40	4.85±0.25	5.03±0.30	4.62±0.24	4.72±0.24	4.81±0.28	4.92±0.25	4.82±0.17	4.86±0.19	4.91±0.25	4.94±0.20
Range	4.18-5.19	4.36-5.24	4.37-5.26	4.72-5.73	4.13-4.90	4.26-5.01	4.28-5.10	4.51-5.34	4.50-5.02	4.51-5.10	4.63-5.17	4.65-5.20
Variance	0.06	0.16	0.06	0.09	0.06	0.06	0.08	0.06	0.03	0.04	0.04	0.04
50-100 (cm) Depth												
Mean	4.21±0.11	4.28±0.10	4.35±0.09	4.53±0.10	4.16±0.12	4.19±0.12	4.31±0.10	4.42± 0.10	4.27± 0.12	4.30± 0.12	4.41± 0.11	4.47± 0.10
Range	4.12-4.45	4.19-4.48	4.25-4.55	4.39-4.69	4.00-4.41	4.01-4.43	4.10-4.47	4.32-1.69	4.08-4.45	4.16-4.46	4.24-4.60	4.33-4.62
Variance	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01

(With some exceptions in 1 M KCl and water soil suspensions). This is in agreement with Black *et al.*[13]. The slight increase in pH of the soil suspensions upon dilution is thus a direct corollary of the observed decrease in pH of the suspension upon addition of neutral salts such as a salts used in this work. At each sampling point, the pH is in the order 0-50 cm > 50-100 cm depths. This might be due to the fact that the area of study is a rain forest region where there is frequent high rate of leaching resulting in protonated clay which will normally decrease the pH of the soils which is in agreement with Fergusson[8].

$$\text{E.g. Clay} - \text{H} + \text{H}_2\text{0} \rightleftarrows \text{Clay}^- + \text{H}_3\text{0}^+$$

The mean pH values for all the soil suspensions fall between 4.21-5.03 with small values of variance. This indicates that the soils are acid soils which are usually associated with humid region[8].

CONCLUSIONS

The mean pH values obtained for all the soil samples fall with in the range of 4.21-5.03. The soils of the study area are therefore strongly acidic. This is because the environment is a humid (rain forest) region where leaching frequently takes place as a result of heavy rainfall. This type of soil is typical of some soils of Southern, South Eastern and South western parts of Nigeria with pH ranging from 4.0-6.0. This type of soils usually supports a wide variety of tree crops and forest trees of economic importance viz; oil palm, rubber, cocoa, coconut, raphia, citrus, kola nut, banana and plantain[14]. The high acidity of the soils can not be linked to anthropogenic influences because the place is not an industrial area. In the process of bituminous sands exploitation, if the tailings (mineral matter and water with dissolved substances) are not treated before discharge, may alter the acidity of the host environmental soils. This will in turn alter the ecology (population of microbes, plants and animals) of the host environment.

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