

Chemical Characterisation of Sludge Generated from Water Treatment Plants (WTPs) in Nigeria

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Abstract

Sludge collected from four (4) selected water treatment plants in Nigeria was characterised chemically to ascertain its compositions and possible usefulness. The results indicated variations in physicochemical, nutrients, essential and non essential metals, and polycyclic aromatic hydrocarbons (PAHs) load among the studied stations. Ranges of mean values of physicochemical parameters were: pH (7.2 – 8.1); electrical conductivity (480.0 – 988.0 μSCm^{-1}); moisture content (12.8 – 24.6%); total organic carbon (6.9 – 8.9 %); ash (8.9 – 12.5%); organic matter (88.5 – 91.1%); total solid (206.5 – 689.2 mgL^{-1}); total dissolved solids (78.2 – 439.8 mgL^{-1}); total suspended solids (104.6 – 183.5 mgL^{-1}); nitrogen (8.6 – 13.4 %); phosphate (0.6 – 2.4 mgL^{-1}); ammonium ion (1.6 – 6.1 mgL^{-1}); nitrate (6.9 – 14.9 mgL^{-1}); and total PAHs (0.2 – 7.7 mgkg^{-1}). Essential elements had mean ranges of 171.0 – 1219.7 mgkg^{-1}K , 5623.3 – 15,821.5 $\text{mgkg}^{-1}\text{Mg}$, 97,342.1 – 354,855.2 $\text{mgkg}^{-1}\text{Ca}$, 273.5 – 432.0 $\text{mgkg}^{-1}\text{Na}$, 8,548.1 – 15,316.6 $\text{mgkg}^{-1}\text{Fe}$, while non essential (trace) elements such as As, Cd, Co, Si and Pb were not detected in all the studied samples. The parameters evaluated were found to be within maximum permissible limit expected for sludge from water treatment plants by United States Environmental Protection Agency (USEPA). These findings reveal that the variation in levels of these properties (physicochemical, nutrients, essential and non essential elements, and PAHs) are largely dependent on the source of raw water used, and the method of treatments. However, the results indicated that sludge from the selected water treatment plants are rich in plant nutrients and can be exploited in the area of soil conditioning and plant fertilizer.

Keywords Water treatment plants, sewage sludge, physicochemical properties, poly-aromatic hydrocarbons, characterisation

Introduction

Sludge is defined as residue or waste generated from the treatment of waste water. [1] The composition and properties of sludge depend on the quality of raw water and the type of treatment processes. They are principally divided into two viz: primary and secondary with the former constituting of materials

collected from primary settling tanks usually employed in waste treatment plants, while the later also called biological sludge constitutes the sludge generated from biological treatment of the wastewater drained from settling tank. [2]

Sludge is an inevitable by-product of waste water treatment and is being produced massively in Nigeria as a result of increase in municipal water treatment facilities. Although, there is no statistic as regarding the number of water

treatment plants in Nigeria, it is observed that very many companies that use water as raw materials for production or services have water treatment plants including State water corporations in all the thirty six States including the Federal Capital Territory. As a result of these proliferations of water treatment plants (WTPs), several tones of sludge are generated annually and its production is expected to increase. However, there are no documented management protocols or legislation on the management of sludge in Nigeria – a situation that has made the substance to be spread on landfills, or stored in the open as the only available option of disposal.

The contents of sludge are complex as they reflect all the substances that are used in the community, where the raw water is sourced which means that there is a vast variation of substances. Apart from the substances that enters the treatment plant, of which some will sediment directly in the mechanical treatment, the sludge will also contain micro organisms produced in the biological treatment step and added chemicals used in the chemical treatment step. Reminders from pharmaceuticals such as antibiotics and hormones in the influent wastewater are other substances that eventually will end up in the sludge. [3] Thus, metals, living organisms, organic substances and nutrients are all mixed together. Sludge has two main components; the liquid and solids components. The liquid phase contains water and also dissolved substances. These may be organic substances in the form of carbohydrates and fatty acids, and inorganic salts such as ammonium. The solid phase contains organic and inorganic matter. [4]

Several authors have reported on the utilization of sludge from water treatment plant in different applications namely soil conditioner and plant fertilizer [5, 6, 7, 8], bio-fuel [9, 10, 11] Bricks for cement production [12], construction materials [13, 14, 15], electricity production [16, 17, 18], biosorbent [19, 20], bio-pesticides [21], bio-plastics [22], bio-enzymes [23], volatile acids like acetic acid, formic acid and propionic acid [24] and others.

In lieu of these enormous applications, and with no reports regarding the characterisation of sludge from water treatment plants in Nigeria, there is need to assess the chemical status of this substance with the intention of exploring its huge potentials. This study therefore, is aimed at characterising sludge from selected water treatment plants (WTPs) in Nigeria. It is also hope that information derived from this study will provide guidelines towards establishing policy and legislation on sludge management in Nigeria. It will also provide baseline information for future research studies about sludge in Nigeria.

Materials and method

Sample collection

Sludge samples were collected from four (4) wastewater treatment plants in Nigeria; namely, a Water Treatment Plant, Bwari, Abuja (Station 1), Akwa Ibom Water Company (Station 2), a Water Treatment Plant in a five star hotel in Uyo, Akwa Ibom State (Station 3), and a Water Treatment Plant in a Brewery company located in Uyo, Akwa Ibom State (Station 4). Samples for physicochemical, nutrients and metals analyses were collected using polyethylene sample bottles with cap, while those for poly-aromatic hydrocarbons (PAHs) were collected using 250 mL amber bottles. All samples were immediately transported to the laboratory for analysis.

Sample pre-treatment and preparations

Prior to analysis, sludge samples for physicochemical and nutrients analyses were filtered and the filtrate stored in a refrigerator at 4°C to avoid degradation of the nutrient and other constituents. [25, 26] Samples for metal analysis was acidified by adding 2mL HNO₃ to pH of 2 or less to prevent the precipitation of metals and converting the metals available to the same oxidation state before being stored in a refrigerator at 4°C for metal analysis. [27] Prior to digestion, the samples were dried in an oven at temperature of 105°C for 6 hours to eliminate water and other liquids and then passed through

a 2 mm sieve to eliminate roots, stones, plastics, grass and other impurities. The samples were then desegregated to fine sizes using mortar and pestle and thoroughly mixed to achieve homogeneity. The powdered samples were then sieved mechanically to obtain fractions that were approximately 60 μm and stored in a polyethylene bag which was put in an air tight container. Samples for the determination of poly-aromatic hydrocarbon were acidified to a $\text{pH} < 2$ before preservation in a refrigerator at 4°C . [28]

Sample analysis

Physicochemical properties and Nutrients

The analyses of physicochemical and nutrient properties of sludge samples were carried out in triplicate. The parameters determined included: pH, temperature, turbidity, electrical conductivity (EC), moisture content, ash and organic matter contents, total organic carbon (TOC), volatile and non-volatile substances, total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), sludge settle volume, sludge settling rate, sludge index, sludge density index, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Nutrients properties included phosphate, nitrate, ammonium ion, sulphate, total kjeldahl nitrogen, and chlorides.

The pH and electrical conductivity of the samples were measured using portable meters after calibration with standard solutions. Moisture content was determined by weighing 100 g of a well mixed sample into a pre-weighed crucible, and heated in an oven at 105°C for 24 h. For ash and organic matter content, 100 g of the sample was measured into a crucible. The crucible was then put in a muffle furnace (CONTROLS model 10 -D1418/A) at the temperature of 500°C for forty (40) minutes. The crucible was removed and cooled in a dessicator and then reweighed. The difference in the weight gave the ash content where organic matter content was hitherto deduced. Total organic carbon (TOC) was determined by Walkely-Black wet oxidation method [29], total

solids, total dissolved solids and total suspended solids, BOD and COD were determined following standard protocols. [30 - 31] Sludge settle volume (SSV_{30}), settling rate, sludge index and sludge density index were determine by pouring 1 L of the fresh sludge into a graduated cylinder and allowed to settle for thirty (30) minutes. The SSV_{30} was measured at the separated line between the sediment and the supernatant. Sludge index was calculated as the ratio between the settled volume and dry residue, while the density index was calculated as the reciprocal of sludge volume index multiplied by 100. [32]

For nutrients, phosphate content of sludge was determined using stannous chloride method 4500-PD, nitrates content by calorimeter methods, while sulphate and chloride contents were determined using turbidimetric method 4500 and titrimetric method respectively (Lenores et al., 2014). For the determination of total kjeldahl nitrogen, 1 g of sample was accurately weighed into a standard 250 mL kjeldahl flask containing 1.5 g CuSO_4 and 1.5 g Na_2SO_4 as catalyst and 5 mL concentrated sulphuric acid. The flask was placed on a heating mantle and was heated gently to prevent frothing for some hours until a clear bluish solution was obtained. The digested solution was allowed to cool and then quantitatively transferred to 100 mL standard flask and make up to the mark with distilled water. Two hundred milliliters (200 mL) portion of the digest was pipetted into a semi micro kjeldahl distillation apparatus and treated with equal volume of 40% NaOH solution. The ammonia evolved was steam distilled into a 100 mL conical flask containing 10 mL solution of saturated boric acid to which 2 drops of Tarhirus indicator (double indicator) had been added. The tip of the condenser was immersed into the boric acid double indicator solution and the distillation continued until about 2/3 of the original volume. The tip of the condenser was rinsed with a few millimetres of distilled water in the distillate which was then titrated with 0.1M HCl until a purple end point was observed. The blank determination was also carried out in a similar manner as described above except for the

omission of the sample. [33] Nitrogen content was then calculated using the relationship

$$\% \text{ Nitrogen} = \frac{\text{Vol.} \times \text{Molarity of acid} \times 0.014 \times \text{Vol. of digest} \times 100}{\text{Weight of sample} \times 10}$$

Determination of essential and non essential metals

A total of fourteen (14) metals were determined in sludge samples from the four stations. The elements were categorized into essential macro elements: potassium (K), magnesium (Mg), calcium (Ca), sodium (Na); essential micro elements: aluminium (Al), copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), and non-essential elements: silicon (Si), arsenic (As), chromium (Cr), cadmium (Cd), and cobalt (Co).

Prior to analysis, 1.00 g sample each was placed in a crucible and 10 mL of aqua regia (HCl / HNO₃ 3:1) added. The solution was left to digest under reflux for an hour and then evaporated to dryness at a temperature of 120°C on a hot plate under a fume hood [9]. The samples were then leached with 5mL HCl and made up to a 10 mL mark before transferring them quantitatively into small sample bottles for atomization using inductively couple plasma optical emission spectrophotometer (Perkin Elmer Optima 5300 DV). To check the accuracy and precision of the method, standard reference material (SRM) 1643e from the National Institute of Standards and Technology (NIST) USA, was used. The results were in good agreement with the NIST certified values (data is not shown). Acidified deionised water was used as a procedural blank while the quality of laboratory analysis was checked by Continuing Calibration Verification (CCV) at 20 and 50 mgkg⁻¹ after every measurement. The concentrations of the elements in the sludge samples were expressed in milligram per kilogram (mgkg⁻¹).

Determination of poly-aromatic hydrocarbons by GC-MS

Poly-aromatic hydrocarbon content in sludge samples were determined following a modified method by Hussein et al. [34] The homogenized

samples were fortified with surrogate standard solution and saponified with 45 mL methanolic KOH. After repeated extraction in n-hexane, further clean up was carried out using a silica-SPE cartridge. The extract was concentrated to a 1 mL volume and analysed by GC-MS using Agilent 7890 gas chromatograph with a 5975C Inert Triple Axis mass selective detector. The instrument detection limits (IDLs) were obtained as concentration of targeted compounds in a sample that results in peaks with signal –to-noise (S/N) ratio of 3:1. The IDL for the GC-MS set up ranged between 0.01 and 0.03 µg/L for individual PAHs. The derivation of the limits of detection (LOD) and quantification (LOQ) was based on the standard deviation of the response (α) and the slope of the calibration curve (S) at levels approaching the limits according to the expressions: LOD = 3.3(α /S) and LOQ = 10 (α /S). The LOD and LOQ values derived for standards of the target compounds were ranged from 0.05 – 0.22 and 0.05-0.19 µg/L, respectively. Concentrations below the IDL were denoted as less than method detection limit (< MDL)

Results and Discussions

Physicochemical properties of sludge

Result of physicochemical properties of sludge samples from the four Stations are presented in Table I. From the result, the mean pH ranged from 7.2 - 8.05, with the highest value (8.1) in Station 2 and lowest (7.2) in Station 1. Turbidity (NTU) ranged from 22.0 – 182.9 with Station 1 recording the lowest (22.0) and Station 4 having the highest (182.9), while electrical conductivities (µSCm⁻¹) ranged from 480 – 988 with the highest value (988.0) recorded in sample from Station 3 and least (480.0) for sample from Station 2. The samples were basic in nature due to the use of calcium hydroxide Ca(OH)₂ and other liming agents in water treatment. The pH of the sludge samples were within the permissible limit of (6.5 – 9.0). The variation in the results of electrical conductivities may be due to different degrees at which metallic salts and complexes of organic matter in the sludge were formed. [35] Results

for moisture, ash, and organic matter contents indicated mean ranges of 12.8 – 24.6%, 8.9 – 12.5% and 88.5 – 91.7% respectively. Sample from Station 1 had the highest (24.6) moisture content, while Station 2 had the lowest (12.5) value. The lowest moisture content in Station 2 may be as a result of the longer period of time in which the sample was left outside prior to sample collection. The variation in organic matter contents of the sludge may be traceable to the different sources of raw water used by these Stations prior to treatment. Although there is no limit to level of organic matter in terms of standard, more than 50% of solid in sludge are organic, and the amount depends on the source of raw water. [36]

Total solids (TS) and total dissolve solids (TDS) measured in mgL^{-1} revealed the following ranges (206.5 – 481.7) and (78.2 – 481.7) and were abundant in the order Station 3 > Station 4 > Station 1, while the range for total suspended solids (mgL^{-1}) was (104.6 -183.5) in the order of Station 3 > Station 1 > Station 4. These three parameters were not determined for sample from Station 2, because the sample was whitish crystal solid at the time of sampling due to non operation of the treatment facility during the period of this study. The variations in TS, TDS and TSS may be as the result of differences in the nature of the samples. Sample from Station 3 was more concentrated in terms of composition of solid characterised by the presence of food wastes. The results for TS, TDS, and TSS obtained in this study are lower than the permissible limit (2500, 1500, 5000 mgL^{-1}) respectively expected for sludge from water treatment plants by United States Environmental Protection Agency (USEPA).

Settle sludge volume (SSV) ranged from 650.0 - 900.0 mL, while settling rate (SR), settle index (SI), sludge density index (SDI), ranges were 0.1 - 0.4, 1.4 - 1.5, 55.9 - 64.4, respectively. SSV is used to determine the health of the floc as well as the severity of poor settling (bulking) episode. The results of these parameters indicated that sample from Station 3 had the highest (900 mL) of solids that settled after 30 min (SSV30), while sample from Station 4 had the lowest (650 mL).

Settling rate of the samples indicated that sample from Station 4 settled faster (0.4) than others which had rate of 0.3 (Station 1) and 0.1 (Station 3). SI recorded the following trend: Station 3 > Station 1 > Station 4 while SDI was in the order Station 4 > Station 1 > Station 3. These variations in SSV30, SI, SDI, and SR are as a result of variation in temperature, sampling and solid content, dimension of settling column and time between sampling and start of analysis [18].

Biochemical oxygen demand (BOD) levels in sludge showed a range (16.0 – 25.0 mgL^{-1}), with sample from Station 3 recording the highest (25.0 mgL^{-1}), while Station 1 had the lowest (16.0 mgL^{-1}). Although, the results for all the samples are within the United State Environmental Protection Agency (USEPA's) permissible limit (30 – 50 mgL^{-1}), however, variations among samples were due to different amounts of organic matter in the sludge. Higher values may be as a result of discharge of sewage effluent into ponds where the sludge was stored as was the case in station 3 in which the sludge was stored in an open pond. Chemical oxygen demand (COD) level varied from 755.0 mgL^{-1} (Station 2) to 976.0 mgL^{-1} (Station 1). This variation was due to differences in the amount of oxidizable organic substances in the samples. However, the obtained results for all the samples analysed showed that COD levels were below maximum permissible limit (> 200 mgL^{-1}) for sludge. [37]

Nutrient levels of sludge

The results for nutrients level of sludge obtained in this study is presented in Table I. The mean ranges for phosphate, nitrate and ammonium ion measured in mgL^{-1} were 0.6 – 2.4, 6.9 – 16.1 and 1.4 – 6.6 respectively. For phosphate, Station 3 recorded the highest (2.4) while the lowest was recorded for sample from Station 2, for nitrate, Station 4 recorded the highest (16.1) and the lowest (6.9) for sludge from Station 2. Station 3 also recorded the highest value (6.6) in terms of ammonium ion content while Station 2

recording the lowest (1.4). In terms of nitrogen content, the range was 8.6 – 13.4% with Station 3 recording the highest (13.4) and the lowest in sludge from Station 2. The reason for these variations in the levels of phosphate, nitrate, ammonium ion and nitrogen in sludge samples may be as a result of varied amount of nitrogenous compounds in the raw water used by these Stations. Wastewater is usually characterised by the presence of large amount of nitrogenous compounds (from faeces, urine, and vegetative waste), which are mostly microbial proteins that can be easily mineralised into ammonia. [38]. The low level of these nutrients in sludge from Station 2 may be traceable to the fact that the sample was left over a long period of time in an open environment exposed to sunshine, rainfall and other agents of denudation, a situation that may lead to leaching or denaturing of the sample before collection. However, the levels of phosphate, nitrogen, ammonium ion and nitrate obtained in this study were all fall within the USEPA's permissible limit for sludge.

Sulphates showed enhanced level in Station 3, recording the highest (15.0 mgL^{-1}), while Station 2 recorded the lowest (4.0 mgL^{-1}). The results for chloride showed that apart from Station 3 that recorded chloride level of 0.5 mgL^{-1} , Stations 1, 2 and 4 recorded same chloride level (0.4 mgL^{-1}). Chloride contents in the samples were very low and within the permissible limit (250 mgL^{-1}). The presence of chlorides is indicative of the use of chloride compounds in the treatment process of each treatment plant, either as coagulants or for the removal of color, organic materials and arsenic.

Table 1: Levels (mean \pm SD) of physicochemical parameters and nutrients in sludge samples from four water treatment plants (WTPs) in Nigeria.

| Parameters | Station 1 | Station 2 | Station 3 | Station 4 | USEPA standard for sludge |
|--|-------------------|-------------------|-------------------|-------------------|---------------------------|
| Physicochemical | | | | | |
| pH | 7.2 \pm 0.20 | 8.1 \pm 0.60 | 7.4 \pm 0.26 | 7.8 \pm 0.46 | 6.5 – 9.0 |
| Temperature ($^{\circ}$ C) | 29.0 \pm 2.01 | 27.0 \pm 2.33 | 27.5 \pm 1.75 | 27.2 \pm 1.62 | Ambient |
| Turbidity (NTU) | 22.0 \pm 1.00 | ND ^b | 156.4 \pm 13.18 | 182.9 \pm 14.21 | > 20 |
| ^a EC (μ S cm^{-1}) | 520.0 \pm 5.13 | 480.0 \pm 11.43 | 988.0 \pm 10.10 | 640.0 \pm 5.01 | < 1000 |
| Moisture content (%) | 24.6 \pm 1.93 | 12.8 \pm 1.10 | 18.7 \pm 2.21 | 20.2 \pm 1.43 | 0 – 25 |
| Ash content (%) | 8.9 \pm 0.43 | 12.5 \pm 0.24 | 9.2 \pm 0.96 | 11.5 \pm 0.65 | - |
| Organic matter (%) | 91.7 \pm 0.00 | 88.5 \pm 0.00 | 90.8 \pm 0.00 | 88.5 \pm 0.00 | - |
| Total Organic Carbon (%) | 6.9 \pm 0.42 | 8.9 \pm 0.84 | 8.6 \pm 0.26 | 7.5 \pm 0.21 | - |
| Volatile substance (%) | 17.7 \pm 1.45 | 12.3 \pm 0.70 | 8.2 \pm 1.11 | 10.6 \pm 0.21 | - |
| Non volatile substance (%) | 82.3 \pm 0.00 | 87.7 \pm 0.00 | 91.8 \pm 0.00 | 89.4 \pm 0.00 | - |
| Total solids (mgL^{-1}) | 206.5 \pm 26.05 | ND ^b | 689.2 \pm 18.63 | 481.7 \pm 11.00 | 2500 |
| Total dissolved solids (mgL^{-1}) | 78.2 \pm 4.23 | ND ^b | 439.8 \pm 12.10 | 243.8 \pm 8.43 | 1500-10,000 |
| Total suspended solids (mgL^{-1}) | 112.2 \pm 18.43 | ND ^b | 183.5 \pm 11.65 | 104.6 \pm 6.98 | > 5000 |
| Settle sludge volume (mL) | 750.0 \pm 10.00 | ND ^b | 900.0 \pm 18.00 | 650.0 \pm 6.21 | - |
| Settling rate | 0.3 \pm 0.01 | ND ^b | 0.1 \pm 0.00 | 0.4 \pm 0.01 | - |
| Sludge index | 1.5 \pm 0.03 | ND ^b | 1.8 \pm 0.04 | 1.4 \pm 0.02 | - |
| Sludge density index (%) | 64.4 \pm 2.66 | ND ^b | 55.9 \pm 1.73 | 73.5 \pm 1.39 | - |
| ^c BOD (mgL^{-1}) | 16.0 \pm 1.42 | ND ^b | 25.0 \pm 2.46 | 18.0 \pm 1.52 | 30 – 50 |
| ^d COD (mgL^{-1}) | 976.0 \pm 12.32 | 755.0 \pm 16.31 | 895.0 \pm 11.85 | 894.0 \pm 10.42 | > 200 |
| Nutrient | | | | | |
| Phosphate (mgL^{-1}) | 1.6 \pm 0.11 | 0.6 \pm 0.01 | 2.4 \pm 0.03 | 1.9 \pm 0.11 | 10 – 25 |
| Nitrate (mgL^{-1}) | 10.5 \pm 1.21 | 6.9 \pm 0.13 | 14.9 \pm 2.12 | 16.1 \pm 1.55 | 50 |
| Ammonium ion (mgL^{-1}) | 2.2 \pm 0.20 | 1.4 \pm 0.02 | 6.6 \pm 1.41 | 4.1 \pm 1.00 | 25 – 45 |
| Sulphate (mgL^{-1}) | 8.0 \pm 1.01 | 4.0 \pm 0.17 | 15.0 \pm 2.11 | 12.0 \pm 1.27 | 500 |
| Nitrogen (%) | 10.6 \pm 1.26 | 8.6 \pm 1.32 | 13.4 \pm 1.68 | 11.8 \pm 0.90 | 10 – 20 |
| Chloride (mgL^{-1}) | 0.4 \pm 0.00 | 0.4 \pm 0.01 | 0.5 \pm 0.00 | 0.4 \pm 0.10 | 250 |

^a -Electrical conductivity, ^c - Biochemical oxygen demand, ^d - Chemical oxygen demand, ^b - Not determined

Essential and non – essential metal levels in sludge

The results of concentration of metals in sludge samples from four stations are presented in Table 2. Ranges for essential macro elements in mgkg^{-1} were potassium (171.9 - 1,219.7), magnesium (5,623.3 - 15,821.5), calcium (97,342.1 - 354,855.2) and sodium (273.5 - 432.0). Station 4 recorded the highest (1,219.7) level of potassium, while Station 3 had the lowest (171.9). In terms of magnesium, highest value (15,821.5) was recorded in sludge from Station 3 and the lowest (5,623.3) in sludge from Station 2. For calcium and sodium, the following orders of abundances were obtained Station 3 > Station 4 > Station 1 > Station 2, and Station 2 > Station 3 > Station 4 > Station 1 respectively. The variations in the level of these metals in the sludge samples may be as a result of different composition of the sludge based on treatment processes or storage. The presence of these elements in the samples is a clear indication of the use of chemicals like potash alum, calcium hydroxide, magnesium sulphate in water treatment, and variation in the levels among stations may be due to the amount used. [39]

For the essential micro elements, aluminium content varied from 24,112.3 mgkg^{-1} in Station 1 to 56,180.5 mgkg^{-1} in Station 3, and 3.7 mgkg^{-1} in Station 3 to 977.4 mgkg^{-1} in Station 2 for copper. Iron results also indicated the highest level (15,316.6 mgkg^{-1}) in Station 3 and lowest level (8,548.1 mgkg^{-1}) in Station 2. The

presence of aluminium in sludge is because during water treatment, aluminium hydroxide is used as a coagulant in addition to its abundance in earthen cluster in water and variation in the level may be due to the amount used. The variation in levels of iron obtained in this study may be due to the kinds of materials that are used in the water treatment facilities as most plants make use of iron or steel facilities. Zinc results indicated a range of 65.0 mgkg^{-1} in Station 1 to 286.1 in Station 2 while manganese was highest (3,141.5 mgkg^{-1}) in sludge from Station 3 and lowest (993.0 mgkg^{-1}) in sludge from Station 2. The levels of copper, iron, zinc and manganese recorded in sludge were all below the acceptable limit by USEPA as indicated in Table 2.

The results of non-essential toxic metals (As, Si, Cd, Cr, Co, Pb) of sludge samples are presented in Table 2. The results show that As, Si, Cd, Co and Pb were not detected in all the samples although Station 3 recorded arsenic level of 1.75 mgkg^{-1} . The results for chromium showed that Station 3 had the highest (22.7 mgkg^{-1}) level, while Station 1 had the lowest (9.5 mgkg^{-1}). The presence of chromium in the samples may be attributed to the use of paint pigment in the coating of sludge tank and water treatment facilities in the stations studied. Chromium levels in all the samples were within the acceptable limit (3000 mgkg^{-1}) for sludge as stipulated by USEPA.

Table 2: Levels (mgkg^{-1}) of metals in sludge from four water treatment plants (WTPs) in Nigeria.

| Element | Station 1 | Station 2 | Station 3 | Station 4 | USEPA Standard |
|-------------------------------------|-----------------|-----------------|-----------------|-----------------|----------------|
| Essential macro elements | | | | | |
| Potassium | 932.3 | 578.4 | 171.9 | 1,219.7 | - |
| Magnesium | 13,745.0 | 5,623.3 | 15,821.5 | 13,623.4 | - |
| Calcium | 282,025.0 | 97,342.1 | 354,855.2 | 258,557.8 | - |
| Sodium | 273.5 | 432.0 | 403.6 | 372.5 | - |
| Essential micro elements | | | | | |
| Aluminium | 24,112.3 | 19,059.8 | 56,180.5 | 41,146.9 | - |
| Copper | ND ^a | 977.4 | 3.7 | 7.1 | 4300 |
| Iron | 12,940.0 | 8,548.1 | 15,316.6 | 15,671.4 | 20,000 |
| Zinc | 65.0 | 286.1 | 70.6 | 68.1 | 7500 |
| Manganese | 1,719.5 | 993.0 | 3,141.5 | 2,171.8 | 5500 |
| Non-essential toxic elements | | | | | |
| Silicon | ND ^a | ND ^a | ND ^a | ND ^a | 50 |
| Arsenic | ND ^a | ND ^a | 1.75 | ND ^a | 75 |
| Chromium | 9.5 | 12.4 | 22.7 | 13.5 | 3000 |
| Cadmium | ND ^a | ND ^a | ND ^a | ND ^a | 85 |
| Cobalt | ND ^a | ND ^a | ND ^a | ND ^a | 320 |

^a- Not detected

Levels of Polycyclic Aromatic Hydrocarbons in sludge

The levels of polycyclic aromatic hydrocarbons (PAHs) in sludge collected from four water treatment plants in Nigeria are presented in Table 3. Total PAHs in each of the samples were 0.2 mgkg^{-1} for Station 1, 0.2 mgkg^{-1} for Station 2, 7.7 mgkg^{-1} for Station 3, and 0.5 mgkg^{-1} for Station 4. Generally, the total PAHs in sludge samples were low with sample from Station 3 recording the highest. Benzo[a]pyrene, Benzo[ghi]perylene, Dibenz[a,h]anthracene, and Indeno[1,2,3-cd]pyrene were not found in all the samples analysed. Four, five and six membered ring compounds were generally very low ($0.00 - 0.02 \text{ mgkg}^{-1}$) in the samples from all the stations. However, in Station 3, anthracene was (7.7 mgkg^{-1}), contributing to the high total PAHs value for this station.

The overall results indicate that Station 3 recorded the highest (7.7 mgkg^{-1}), while the

lowest (0.2 mgkg^{-1}) was obtained for sample from Station 1. The variations in total PAHs among the different stations may be due to the source of raw water for the water treatment plants. Anthracene contributed 7.5 mgkg^{-1} to the total PAHs (7.7 mgkg^{-1}) in Station 3. This is because the sludge tank in Station 3 was very close to a generator house. It might have been possible that some of the used oil or leakages from the engine had leached into the storage tanks, contributing to high anthracene in the sample. The presence of PAHs in sludge is as a result of sedimentation of suspended solids during the wastewater treatment and usually contains significant concentrations of many classes of organic contaminants. [40, 41] Also, PAHs may enter a wastewater treatment plant either as part of an industrial discharge, or as a component of domestic effluent drainage from the sewage system and runoff.

Table 3: Levels (mgkg⁻¹) of PAHs in sludge from four water treatment plants in Nigeria

| PAHs | Station 1 | Station 2 | Station 3 | Station 4 |
|------------------------|-----------|-----------|------------------|-----------|
| Napthalene | 0.09 | 0.00 | 0.00 | 0.00 |
| Acenaphthylene | 0.00 | 0.03 | 0.11 | 0.00 |
| Acenaphthene | 0.00 | 0.00 | 0.00 | 0.00 |
| Fluorene | 0.00 | 0.00 | 0.00 | 0.00 |
| Phenanthrene | 0.00 | 0.11 | BDL ^a | 0.21 |
| Anthracene | 0.04 | 0.00 | 7.53 | 0.21 |
| Fluoranthene | 0.00 | 0.00 | 0.00 | 0.00 |
| Pyrene | 0.00 | 0.04 | 0.00 | 0.04 |
| Benz[b]anthracene | 0.01 | 0.00 | 0.00 | 0.00 |
| Chrysene | 0.01 | 0.00 | 0.00 | 0.00 |
| Benzo[b]fluoranthene | 0.01 | 0.00 | 0.00 | 0.00 |
| Benzo[k]fluoranthene | 0.02 | 0.00 | 0.00 | 0.00 |
| Benzo[a]pyrene | 0.00 | 0.00 | 0.00 | 0.00 |
| Benzo[ghi]perylene | 0.00 | 0.00 | 0.00 | 0.00 |
| Dibenz[a,h]anthracene | 0.00 | 0.00 | 0.00 | 0.00 |
| indino[1,2,3-cd]pyrene | 0.00 | 0.00 | 0.00 | 0.00 |
| Total | 0.17 | 0.18 | 7.64 | 0.46 |

^a – Below Detected Limit

Conclusion

This study has revealed that sludge from the selected water treatment plants in Nigeria contained varied physicochemical properties, nutrients, essential and non essential elements, and polyaromatic hydrocarbons load. The levels of these properties are largely dependent on the source of raw water used and the method of treatments. Sludge was rich in nutrients (phosphate, nitrate, ammonium ion and nitrogen), but not exceeding the permissible limit expected for sludge from water treatment plants. They were also rich in essential (macro and micro) elements while non essential (trace) elements were not detected. The sludge was not overloaded with PAHs as most compounds recorded a zero to below detectable levels. The non detectable level of non essential elements and low PAHs recorded in sludge are good

attributes that can be explore in its utilization in land application, plant fertilizer, or any other applications.

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