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EFFECT OF PYROLYSIS TEMPERATURE ON PROPERTIES OF SLUDGE FROM WASTEWATER TREATMENT PLANT IN NIGERIA

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ABSTRACT

Physicochemical properties, nutrients, structural and morphological characteristics of biochar derived from sludge collected from Lower Usuma Dam Wastewater Treatment Plant in Nigeria at different pyrolytic temperatures were investigated. Results showed significant variations in physicochemical and nutrient levels of biochar with temperature. Hydrogen ion concentration, ash and volatile matter levels were directly proportional to temperature, while biochar yield, moisture and organic content were indirectly proportional to temperature. Nitrogen, nitrate, ammonium ion and chlorides all decrease with temperature, while sulphate and phosphate of the biochar increase with temperature. Elemental analysis results indicated essential macro elements (Ca, Mg, K, Na), essential micro elements (Al, Zn, Fe, Mn) all increased with temperature due to the ability of the samples to concentrates by gradual loss of carbon, hydrogen and oxygen (CHO). X-ray diffraction result revealed the presence of $CaCO_3$ and SiO_2 in all the samples with Brunauer-Emmett Teller surface area and pore volume decreasing greatly with pyrolytic temperature. There was similarities in the spectra of all the biochar disregarding temperature differences, although biochar obtained at the highest temperature (700°C) were found to have more spherical round edges with almost even surface than others.

Keywords: Sludge, pyrolysis, physicochemical, biochar, water treatment plant.

INTRODUCTION

Sludge is a bye-product of waste water treatment process and is composed of several constituents including organic compounds, macro and micronutrients, trace elements, micro organism, micro pollutants and others. [1] Recent innovations in environmental applications have focused on improving environmental accountability, either through the use of more sustainable

materials or better management practices, into project design and implementation. Sludge usually undergo various types of processing for economic and hygienic reason and the purpose is to reduce the volume, stabilized the sludge, remove water and kill pathogenic organisms. Several technologies have been evolved and developed for stabilization of sludge including heat treatment (pyrolysis), aerobic and anaerobic digestion, composition and others.[2] Of these several techniques, pyrolysis is frequently used in the treatment of sludge due to its economic and less demands of energy in addition to nutrient recovery, and control of heavy-metal emissions as compared to other methods. [3 - 6]

Pyrolysis is an innovative method developed to manage sludge, wherein the sludge is thermally treated under pressure and in the absence of oxygen. [7] In this method, the sludge is transformed into char (biochar), pyrolysis oils, water vapour, and combustible gases. During pyrolysis, the sludge is stabilised and pathogens are killed and characteristics of sludge are definitely improved for a number of reasons. Fats and oils are dissolved, cell walls of organic particles and organisms are ruptured and thereby releasing their cellular water and finally, extra cellular polysaccharides that bind water are also broken down. [8] Chemically, biochar is difficult to define because of the wide variety of biomass and charring conditions used in its production, which results in materials with a wide range of final characteristics. [9]

Several factors such as process temperature, reaction time or period of pyrolysis, operation pressure and raw materials characteristics have been reported as factors that affect the key functional properties of the resultant biochar, such as sorption characteristics, surface area, porosity and structural arrangement, surface charge and alkalinity, and organic carbon content with pyrolytic temperature being the most critical.[1] Thus, the present study is aimed at investigating the effect of temperature variation on the physicochemical properties, nutrients, structural and morphological properties of biochar derived from sludge from wastewater treatment plant in Nigeria.

MATERIALS AND METHODS

Description of sampling station

Sludge sample was collected from Lower Usuma Dam Water Treatment Plant (LUDWTP), Bwari, Abuja, Nigeria. The LUDWTP is located within the Lower Usuma Water Works in Bwari Area Council at the periphery of Abuja Metropolis. It lies between the Latitude of $8^0$25 and $9^0$25 N and Longitude $6^0$45 and $7^0$45 E with an elevation of 2,000 meters above the sea level. The facility has capacity to process 120 million litres of waste water, delivery portable water to the city of Abuja and its environs. The facility has been in extensive use since 1987 and has in storage several tones of sludge,

The water treatment technology in LUDWTP involves aeration then followed by removal of large solids implementing drum screens. The water then passes through

the lamella sludge blanket clarifier / inclined-plate clarifier in place of conventional settling tanks for clarification. The technology makes use of highly compact settlers, reducing the space requirements compared with the latter by up to 90%. This clarified water is put to rapid gravity filtration by passing it through a filter medium consisting of sand filters, by gravity or under pumped pressure. The filter removes flocculated materials trapped in the sand. Then the water is disinfected in the contact tank with chlorine and goes through chemical dosing using aluminum sulphate, lime, polyelectrolyte and chlorine. Sand filters are cleaned by backwashing, which involves reversing the direction of the water and adding compressed air. Sludge produced is directed into a specific well and then push into lagoons or nearby land. Figure 1 below shows Lower Usuma Dam on the delineated map of Abuja, Federal Capital Territory, Abuja,Nigeria

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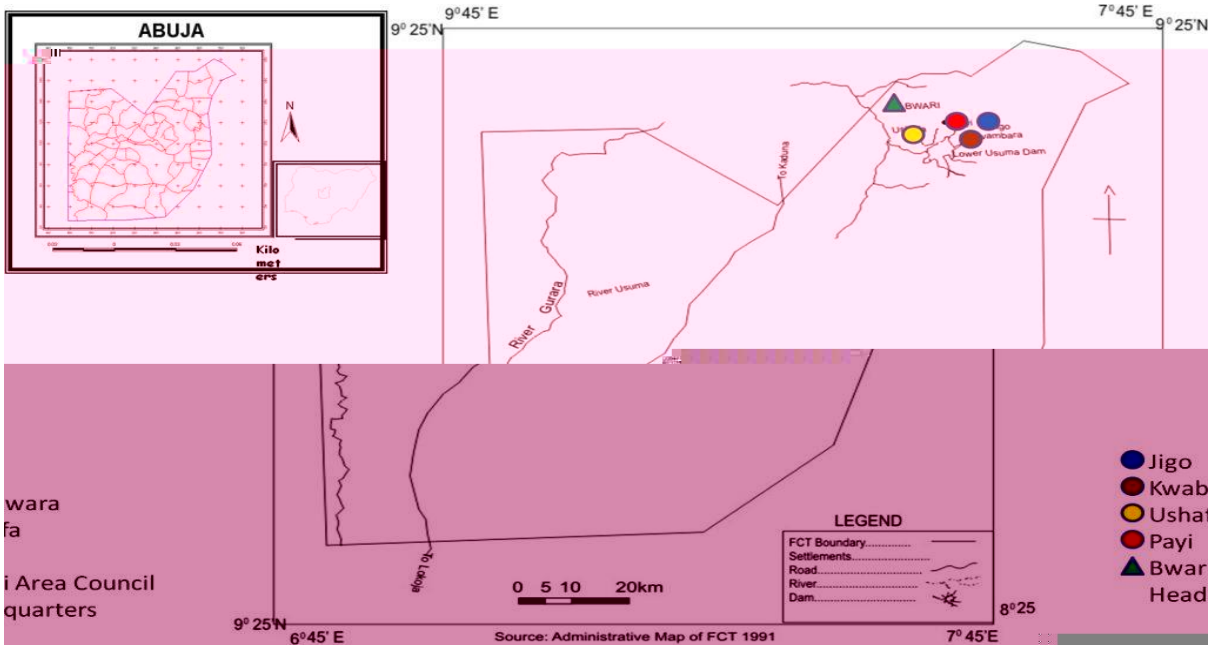

Figure 1: Lower Usuma Dam on the Delineated map of Abuja, Federal Capital Territory

SAMPLE COLLECTION AND PRE-TREATMENT

Grab sludge samples were collected from the study site using standard procedure. The sampling was done three times at a regular interval from the same batch to make a composite sample using a grab sampler before storing in polyethylene sample bottles already rinsed with n-hexane and dichloromethane to remove adhering polar and non-polar compound. [10] All samples were transported in ice-cooled chest to the laboratory for treatment and analysis. The samples were then put in a refrigerator at $4^{o}C$ to avoid degradation of the nutrient and other constituent. [11 12]

BIOCHAR PREPARATION

The sludge was first air dried to constant mass for 48h and then ashed at a temperature range of 200 700°C under pressure in a muffle furnace (model SXL) in an oxygen deficient environment for a residence time of 120 mins for each temperature (Stolarek and Ledakowicz, 2001). The biochar product (ash) derived was cooled in desiccators before storing in polyethylene bags and put in an air tight container for further analysis. Although, during pyrolysis of sludge from water treatment plant, several components such as vapour, biogas, and ash (biochar) are produced, in this study, only the ash component was collected for analysis.

SAMPLE ANALYSIS

Determination of Physicochemical properties and Nutrients of biochar

Physicochemical and nutrient properties of air dried ($0^{o}C$) and biochar samples (200 - $700^{o}C$) were done following standard protocols. The parameters determined included: pH, electrical conductivity (EC), moisture content, ash and organic matter contents, total organic carbon (TOC), volatile substances, and biochar yield. 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 100g each of the biochar sample into a pre-weighed crucible, and heated in an oven at $105^{o}C$ for 24 h. For ash and organic matter content, 100 g of each 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 ^{o}C for forty (40) minutes. The crucible was then 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 by measuring 0.18 g of biochar into Erlenmeyer flask before adding 10 ml potassium dichromate (VI) and mixed thoroughly then followed by addition of 20 ml sulphuric acid. The resulting solution was then diluted with 100ml distilled water and five drops of O-Phenanthrolerie indicator added. The obtained solution was then titrated with ferrous ammonium sulphate to maroon color end point. [13]

For nutrients, phosphate content of sludge was determined using stannous chloride method 4500-PD, nitrates content by calorimeter methods, while sulphate and chlorides contents were determined using turbidimetric method 4500 and titrimetric method respectively. [14] For determination of total kjeldahl nitrogen, 1g 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 5ml 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 (200ml) portion of the digest was pipetted into a semi micro kjehdahl 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 Tarhirus indicator (double indicator) has been added. The tip of the condenser was immersed into the boric acid double indicator solution and then the distillation continue 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. [15 16] Nitrogen content was then calculated using the relationship below.

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

Determination of metals in biochar

A total of fifteen (15) metals were determined in sludge collected from the station. 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), chromium (Cr), cadmium (Cd), cobalt (Co), arsenic (As) and lead (Pb).

Prior to analysis, 1.00 g sample each was placed in a crucible and 10 ml using aqua regia (HCl / HNO_3 3:1) added. The solution was then 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. [12] 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 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 50mgkg^{-1} after every measurement. The concentrations of the elements in the sludge samples were expressed in milligram per kilogram (mgkg^{-1}).

Characterisation of biochars

Beside the determination of physicochemical, nutrients and metal levels in air dried sample and biochar obtained from pyrolysis of sludge from water treatment plants, the air dried sample and biochar were also subjected to further characterisation to evaluate the influence of temperature changes on structural and morphological properties of the obtained biochars.

Determination of Surface Area and Porosity Characteristics

Surface area and porosity characteristics of biochar were done using nitrogen adsorption principle at -196°C using Tristar 3000 surface area and porosity analyzer (Micromeritics, USA). Prior to analysis, the samples were evacuated at 300 ^{o}C for 3 hours in order to clean the surface of the samples of any adsorbed impurities like gas and water vapour. The surface area was calculated using Brunauer-Emmett-Teller (BET) model. The PSD of the samples was calculated using Barett-Joyner-Halenda (BJH) method from desorption branche. Total volume of micropores and mesopores were calculated from the amounts of nitrogen adsorbed at P/Po = 0.993.

Determination of Functional Group

The functional group analysis was done using Fourier Transform Infrared Spectroscopy (FTIR) spectrophotometer (Nicolet 6700, USA). Before the analysis, samples were prepared by mixing 1 mg of the dried specimen with 200 mg KBr (Merck, for spectroscopy) in an agate mortar and then the resulting mixture was pressed into KBr pellet under vacuum. The spectra were recorded after 64 scans from 600 to 4000 cm^{-1}.

Determination of Phase Purity and Crystalinity

Samples were milled into fine powder and were pressed into the sample plates and, then mounted to the sample holder of the x-ray d
PRO, X-ray diffractometer). XRD patterns were obtained using a Cu Ka radiation generated at 40 kV and 40 mA. The 2 range was scanned from 5 to 75° at a speed of 10°/ min.

Determination of Surface Morphology

Prior to analysis, samples were dispersed in acetone and sprayed on a glass slide to evaporate the acetone. The fine powder samples were then sprinkled on a carbon tape and focused with the microscope. The

accelerating voltage of the microscope (S-4800 scanning electron microscope, Japan HQ) was 0.5 30kV.

RESULTS AND DISCUSSIONS

Physicochemical and Nutrient Levels in air dried and biochar samples

The results of physicochemical properties and nutrients levels of air dried and biochar obtained from Lower Usuma Dam Water Treatment Plant (LUDWTP) at 200 ^{o}C - 700 ^{o}C are presented in Table 1. For the physicochemical parameters, ranges were pH 7.2 - 9.7, with the highest value (9.7) in biochar produced at 700°C and lowest (7.2) in the air dried (0°C) sample. Electrical conductivity ranged from 194.0 - 520.0 µSCm^{-1}, with sample at 0°C recording the highest (520.0) and biochar produced at 300°C recording the lowest (194.0). The result indicated an increase in pH with increasing temperature among the biochar samples and this may be due to the relative concentration of non pyrolysed inorganic element present in the original sludge sample. Also, during pyrolysis, there is a release of acidic surface groups as temperature increases, while the basic groups are still present. [17] For electrical conductivity, although the result did not show a particular trend with temperature, the variations obtained in the result may be due to the varying amount of water soluble ions present in the biochar. Moisture content ranged from 5.8 24.6% with biochar produced at 0°C recorded the highest (24.6) and the lower (5.8) recorded in biochar produced at 700°C. Ash content revealed a range of 3.9 10.5% in the order of 700°C > 600°C > 500°C > 400°C > 300°C > 200°C > 0°C, organic matter recorded a range of 89.4 96.7% with biochar produced at 0°C recorded the highest (96.7) and biochar produced at 700°C recorded the lowest (89.4), while volatile matter indicated a range of 2.5 12.2% with similar trend of increasing with increased temperature obtained for pH and ash (Table 1). These results (ash content, organic matter, and volatile matter) can be explained by the fact during pyrolysis, as temperature increases, organic matter content of biochar is burnt off and gradually converted to ash. The variation in moisture content indicated in the biochar is due to the loss of organic materials and water content in the biochar during high temperature heating leading to reduction in their levels. Total organic carbon showed a range of (6.9 13.9) with biochar obtained at 500°C recording the highest (13.9) value and lowest (6.9) in biochar obtained at 0°C, while biochar yield had range from 24.6 61.2% with decrease abundance as temperature of pyrolysis increases.

For the nutrients, the levels of phosphate, nitrate, ammonium ion, sulphate, chlorides and nitrogen are presented in Table 1. The ranges for phosphate, nitrate and ammonium ion measured in mgkg^{-1} were (1.3 4.0); (0.2 8.2); and (0.9 2.4) respectively. For phosphate, biochar produced at 700°C recorded the highest value (4.0), and the lowest (1.3) in sample produced at 0°C, for nitrate, biochar produced at 0°C recorded the highest value (8.2) and lowest (0.2) in

biochar produced at 700°C, while ammonium level revealed the highest value (2.2) in sample obtained at 0°C and lowest (0.9) in biochar obtained at 700°C. The results for sulphate (mgkg^{-1}), chloride (mgkg^{-1}) and nitrogen (%) presented in Table 1 indicated ranges as (8.0 10.6); (< 0.1 0.4); and (< 0.0 9.7) respectively. From the result of nutrient, nitrate, ammonium ion, chloride and nitrogen levels in biochar within the experimented temperatures were inversely related with temperature. The reason may be due to volatilization that may have occurred in the samples during pyrolysis. The results for phosphate and sulphates in the biochar showed increase abundance with temperature suggesting that phosphate and sulphate in the original sludge were associated with the inorganic fraction of the sludge. [18]

Metal levels in biochar

The results for metal level ($mgkg^{-1}$) of air dried samples and biochar pyrolysed at temperatures between 200 700°C are presented in Table 2. Ranges for essential macro elements were potassium (932.3 1,927.8), magnesium (13,745.0 - 17,775.0), calcium (282,025 - 345,175.0) and sodium (243.5 - 445.5). The results indicated that the essential macro elements recorded an increased level with increasing temperature in all the samples. The reason for the obtained trend may be due to the ability of the samples to concentrates due to gradual loss of carbon, hydrogen and oxygen (CHO) during pyrolysis. The high relative proportion of calcium in the samples among the entire essential macro element analysed for, may be traceable to the use of calcium oxide or its compound during process prior to dewatering during water treatment process. Essential micro elements ($mgkg^{-1}$) recorded the following ranges: Aluminium (24,112.3 45,560.0), copper (36.5 76.8), iron (12,940.0 18,383.0), zinc (65.0 100.5), and manganese (1,719.0 2,366.8). There was no established trend in the levels of these elements with temperature of pyrolysis. Biochar obtained at 700°C recorded highest level (45,560.0) of aluminium and lowest level (24,112.3) in biochar obtained at 0°C, while iron recorded the highest value (18,383.0) in biochar obtained at 600°C and lowest value (12,940.0) in biochar obtained at 0°C. Zinc recorded the highest value (100.5) in biochar obtained at 700°C, and lowest (65.0) in biochar obtained at 0°C, while biochar obtained at 600°C had the highest level (2,366.8) of manganese and the lowest (1,719.0) in biochar obtained at 0°C. The variation in the levels of these elements can be explained in terms of the loss in weight of these elements being lower than the loss in weight of organic compounds during pyrolysis which hitherto may have led to the enrichment in the biochar mix. Result for non essential toxic elements show range for silicon (0.8 - 1.5) and chromium (10.2 20.4) with cadmium, cobalt, nickel, lead, not detected in the samples pyrolysed at different temperatures. The reason may be that these elements could be present in the form of smaller molecular compound following pyrolysis, and tends to dissolute and volatilised rather than decomposed for detection. The result for silicon was seen to increase with temperature and is strongly related to the increasing ash content of the biochar which favours the formation of Si-C bond, thereby increasing the number of aromatic compounds and recalcitrancy of the samples. [19]

Table 2: Level ($mgkg^{-1}$) of metals in air dried (0^oC) and biochar obtained from sludge from LUDWTP

Elements	**Samples**						
Essential macro	0^oC	200^oC	300^oC	400^oC	500^oC	600^oC	700^oC
Potassium	932.3	1,200.5	1,207.5	1,268.0	1,462.8	1,727.8	1,972.8
Magnesium	13,745.0	15,795.0	15,538.0	15,687.5	16,322.5	16,762.5	17,775.0
Calcium	282,025.0	313,650.0	315,050.0	316,800.0	323,200.00	331,823.0	345,175.0
Sodium	243.5	260.8	262.0	276.0	280.8	320.8	445.5
Essential micro							
Aluminium	24,112.3	30,992.5	31,837.5	32,337.5	31,495.0	38,697.5	45,560.0
Copper	36.5	42.5	48.0	62.5	66.5	72.8	76.5
Iron	12,940.0	15,590.0	15,300.0	15,885.0	14,950.0	18,383.0	17,318.0
Zinc	65.0	78.8	81.3	91.6	76.8	89.0	100.5
Manganese	1,719.0	2,127.8	2,159.5	2,183.5	2,110.8	2,366.8	2,083.5
Non essential toxic							
Silicon	0.8	1.4	2.9	3.3	3.5	4.0	5.1
Chromium	10.2	13.0	13.5	14.0	13.8	18.8	20.4
Cadmium	ND	ND	ND	ND	ND	ND	ND
Cobalt	ND	ND	ND	ND	ND	ND	ND
Arsenic	ND	ND	ND	ND	ND	ND	ND
Lead	ND	ND	ND	ND	ND	ND	ND

ND Not Detected

Structural and morphological properties of air dried sludge sample and biochar

Phase purity and crystallinity

The result of the x-ray analysis of air dried sample (0^oC) and biochar (200, 500 and 700^oC) is presented in Figure 2. S-A0, S-A200, S-A500, and S-A700 represents air dried, biochar obtained at 200^oC, 500^oC, and 700^oC respectively. The reason for the selective biochars used in the analysis was to represent air dried (S-A0), low temperature (S-A200), high temperature (S-A500) and extremely high temperature (S-A700) scenarios. From the X-ray diffractogram, sharp peaks were observed in all the samples analysed which confirmed the presence of crystalline material ($CaCO_3$) ^{o}. It is observed that the dominant crystal form was calcite for all the samples. With increase in temperature, from 500 700^oC, intensity of $CaCO_3$ peaks shortened due to the decomposition of $CaCO_3$ into CaO eliminating carbon (IV) oxide, and amorphortization during high temperature pyrolysis. However, this leads to slight broadening of the peaks and in effect decrease in crystalline size as shown in the Figure 2. The presence of these compounds in sludge is due to the effectiveness of water treatment plant in removing Ca^{2+} from hard water (owing to source of raw water) before being flushed into drain after treatment. The decomposition of $CaCO_3$ to CaO during high temperature pyrolysis was also responsible for the high pH values of samples pyrolysed at 500 700 ^oC (Table 1) as the sample basicity was mainly linked to the presence of calcium. [1] Biochar also contained relatively small proportion of silicon (IV) oxide as shown in XRD spectra, although absent in the air dried (S-A0) sample.

(a) S-A0 (b) S-A200 (c) S-A500 (d) S-A700

Figure 2: XRD characteristics of air dried (A0) and biochar (200^oC, 500^oC, 700^oC)

less rough when compared to air dried sample.

Conclusion

As a result of the work conducted, it was found that air dried and biochar obtained at different pyrolysis temperatures from water treatment plant in Nigeria differ significantly in physicochemical properties, nutrient levels and metal composition. The study also revealed a significant variation in phase purity and crystallinity, surface area and porosity characteristics, functional group and surface morphology between air dried sludge sample and the obtained biochar processed at different temperature.

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