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Original Research Article

Kinetics Studies of Nitrogen Release by Lixisols, Plinthosols and Acrisols Amended with Modified Oil Palm (*Elaeis guineensis Jacq*) Empty Fruit Bunch

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ABSTRACT

The quest for organic products globally has necessitated the appropriate use of organic wastes that are nutrients-enriching and safe. Hence, this study evaluated the use of four amendments (raw, composted and pyrolyzed oil palm empty fruit bunch as modified forms and NPKMg fertilizer), applied at the rate of 75 kg K ha^{-1} and their effects on the nitrogen release characteristics in three soil types (Lixisol, Plinthosol and Acrisol). The research was carried out at the Ohosu experimental station of Nigerian Institute for Oil Palm Research (NIFOR), Edo State, Nigeria between November 2018 and December 2019. The field experiment was arranged in a randomized complete block design with three replicates. Oil Palm seedlings of ages 3 and 12 months were planted, soil samples were collected and analyzed for NO_3^- and NH_4^+ - nitrogen release monthly. Data collected were subjected to kinetics models (Lagergren pseudo first order, Pseudo second order and Elovich), Analysis of Variance and regression analysis. Treatment means were separated using Least Significant Difference ($p \leq 0.05$). Results showed that Acrisol treated with compost had the highest NO_3^- and NH_4^+ - N release of 1400 mg/kg. The kinetics of NO_3^- , NH_4^+-N - release fitted most to the pseudo second order model for Lixisol and Plinthosol treated with compost, and Lixisol treated with biochar. The kinetics followed pseudo first order model for Acrisol treated with compost. The study observed that treatments and fertilizers had significantly increased the concentration of mineral nitrogen (NH_4^+ and NO_3^- nitrogen) in soil due to net mineralization.

1. INTRODUCTION

The quest for organic products globally has necessitated the appropriate use of organic wastes that are nutrients enriching and safe. This is borne out of the need for farmers to become less dependent on inorganic or chemical fertilizers, thereby reducing the cost of farm inputs. Land applications of organic wastes can improve the physical and chemical properties of soils and provide primary nutrients (nitrogen, phosphorus and potassium) necessary for plant growth (Evanylo *et al.,* 2008). Continued application of primary nutrient sources in amount greater than crop needs result in an accumulation of those nutrients in soil surface horizons (Aduay *et al.*, 2002). High-nutrients organic waste amendments will result in increased mobility of primary nutrient and this is an important issue for managing organic waste applied to soils. When a material containing primary nutrients is applied to soil that initially has low level of nutrients, the soluble forms of the nutrients become increasingly less soluble with time (Akanni and Ojeniyi, 2007). From an agronomic point of view, this is a concern because primary nutrients that are strongly retained by the soil are less available for plant uptake. But from the soil chemist point of view, strong retention of primary nutrients by soil may prevent losses of soluble primary nutrients in runoff as well as movement to groundwater. Thus, the understanding of the nutrient release pattern in soils may play an important role in both the agronomic and soil chemistry aspects of primary nutrients management (Yilangai *et al.,* 2014).

Nitrogen (N) is an essential nutrient required by plants for growth (Hamdi, *et al* 2013). The introduction of organic waste as source of N is considered sustainable and cost effective in modern agriculture to meet the food needs of the global growing population. Nitrate (NO_3^-) is the main N forms in which plants uptake. In view of this, research findings observed that the leaching of nitrate as a result of high rates of fertilization and mineralization of organic N can result in degradation of plant water quality. Water contamination by leaching of nitrate have been traced to outbreaks of infectious disease and its conversion to nitrite in the digestive tracts of infants and ruminant animals, results in poor oxygen circulation by the blood hemoglobin, which could lead to death (Fewtrell, 2004; Hamdi, *et al* 2013).

The capacity of soil to uptake anions can decrease NO_3^- leaching to the deeper soil levels and increase the NO_3^- availability for plant nutrition, which plays a critical part in improving soil nutrition in NIFOR soils, where NO_3^- availability is a limiting factor (Oko-oboh, *et al* 2016). Literature review on previous studies reported the sorption of NO_3^- by soils (Reynolds-Vargas, *et al* 1994; Tani, *et al.* 2004; Hamdi, *et al* 2013). Nevertheless, NO_3^- movement in soils is majorly determined by factors such as the, organic matter content, pH of soil water, concentrations of iron and aluminum oxide concentrations, soil texture and clay mineralogy, competition with other anions as Cl^- and concentration of nitrate in soil water (Qafoku, *et al.* 2000; Panuccio, *et al.* 2001; Donn and Menzies, 2005; Hamdi, *et al.* 2013)

The NO_3^- sorption process has been studied in different soils orders in tropical latitudes, Oxisols, ultisols and in forest soils (Dynia, 2000; Strahm and Harrison, 2006). There is need to evaluate NO_3^- dynamics for NIFOR soils, in particular the Lixisols, Plinthosols and Acrisols, which is a vital oil palm production plantation soils in Nigeria. The aim of this study therefore was to assess the effectiveness of NPKMg fertilizer, raw and modified oil palm empty fruit bunch (biochar and compost) as amendments to release nitrogen in soils of NIFOR Ohosu experimental station.

2. MATERIALS AND METHODS

2.1. Description of Study Site

The study was conducted at the Nigerian Institute for Oil Palm Research (NIFOR) Ohosu Experimental Station in Ovia South West Local Government Area of Edo State, Nigeria. The site is 2,100 hectares, it lies within (Latitudes 6^0 39' 90.8" N and 6^0 39' 74.5"N; and Longitude 5^0 07' 33.3" E and 5^0 09' 46.9" E) with the perimeter map shown in Figure 1. The annual rainfall for the area ranges from 1595 – 2127.2 mm. The area is a transitional rainforest zone dominated by semi-deciduous forest, but due to human interference, the vegetation has been altered over the decades. The present land use is arable with few tree crops (mango, orange, pear, etc) and fallow land with few timbers. The elevation above the sea level ranged from 35 to 70 m with a slope of < 4%. Five soil types were identified in the study area according to Oko-oboh (2016) as Rhodic Kanhanpludalf (Lixisol), Plinthic Kandiudalf (Plinthosol), Aquic Kandiudalf (Acrisol), Aquic Kandiudalf (Luvisol), and Aquic Kandihapludalf (Acrisol).

2.2. Sampling Methods, Analyses and Data Collection

The oil palm empty fruit bunch was collected from the main station of the Nigerian Institute for Oil Palm Research. The bunches were modified into biochar by pyrolysis, compost using cow dung and applied as soil nutrient amendments. The oil palm empty fruit bunch was separated from the palm stalk and reduced to small sizes using shredder. These shredded bunches were loaded into a Biochar Klin pyrolyzer and ignited. The temperature of the pyrolyzer was monitored using infrared thermometer at 350 ^{o}C and left for one hour, thirty minutes to char. The charred empty fruit bunch was then milled to fine powder using a mechanical grinder. The Biochar particles was sieved and characterized for use in analysis.

Compost materials include oil palm empty fruit bunches (EFB), and cow dung. The heap method was used to prepare the compost as follows: the ratio of the cow dung to oil palm empty fruit bunch is 2:1. The EFB was broken down into strips of fiber using a hammer mill shredder. With the EFB being broken down into strips of fiber, the decomposition process of EFB was faster. The shredded EFB was mixed with cow dung manure which is rich in nitrogen in ratio 2:1 and stacked up into rows of compost piles called windrows. The compost was covered with polyethylene sheet to reduce the loss of heat and moisture. The compost was turned once a week after the heap was built and a metal rod is driven into it at the middle. The heap was heated up and then cool down after turning. After the fourth turning stage the heap was ready for use. The product was completed in about 6-10 weeks (Burke *et al.,* 2014).

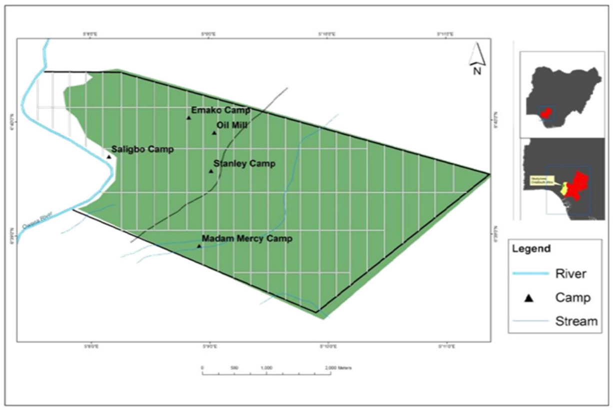

Figure 1: Perimeter map of NIFOR-Ohosu experiment station

2.3. Characterization of Samples

All raw oil palm empty fruit bunch (raw, composted and pyrolyzed) samples were characterized as follows: the biochar obtained was characterized in terms of the following: Percentage yield, pH determination of biochar (potentiometric method) (Chamarthy, 2001), specific surface area (Ishak and Baker, 1995); cation exchange capacity (CEC) (Ma *et al.*, 2010), exchangeable bases (Chamarthy, 2001; Venderbosch and Prins, 2010). The surface functional groups of biochar was measured by using pellet press Kbr disc method through Fourier Transform Infrared (FTIR) Spectrometer (Perkin Elmer Corporation, Norwalk, CT, USA), where the spectra were recorded from 4000 to 500 cm^{-1}, proximate analysis was carried out to study the relative moisture, volatile matters, ash and fixed carbon contents in the biochar samples. The analysis was carried out by following Standard Test Method for Chemical Analysis of Wood Charcoal, ASTM D1762-84 (ASTM, 2007), biochar liming value.

2.4. Physical and Chemical Analyses of Soil

Particle size analysis of the soil was determined by hydrometer method (IITA, 2012). The proportion of sand, clay and silt were used to determine the textural class of the soil using USDA textural triangle. Soil pH was measured in 1:2 soil-water ratio. Soil organic carbon was estimated using the Walkley and Black, (1934) procedure. Total nitrogen was determined by the regular macro-Kjedahl digestion method (AOAC, 2003). Available phosphorus (P) was extracted using Bray-1 method (Ubi *et al.,* 2012) and determined colorimetrically (Ubi *et al.,* 2012) Exchangeable bases (K, Na, Ca, and Mg) were extracted with 1 N ammonium acetate buffered to pH 7.0. K and Na in the extract were determined by flame photometer (Microprocessor Flame photometer-

1381), while Ca and Mg were determined by Atomic Absorption Spectrophotometer (AAS): Perkin Elmer 200 Analyst (B3150060).

2.5. Field Experiment

The field size per soil type was 45 m x 45 m (2025 m^2). This experiment was carried out in the field of NIFOR Ohosu experimental station (Field layout). The field was divided into fifteen experimental plots including controls of size of 9 m x 4.5 m (40.5 m^2) in a randomized complete block design (RCBD) with three replications. Three stands of oil palm seedlings were planted per plot. Treatments were applied 6 weeks after transplanting the seedlings into the field at a spacing of 9 m triangular. The rate of application for raw, composted, pyrolyzed oil palm empty fruit bunch (biochar) and NPKMg fertilizer was 75 kg K ha^{-1}. Data were collected from the field experiment at one month interval for 12 months. Data obtained were used to determine the kinetics of N release in the soil analyzed using the models (the Langergren pseudo first order, pseudo second order and Elovich models).

2.6. Statistical Analysis

Data collected were subjected to analysis of variance (ANOVA) using Genstat-12 software. The significant treatment means were separated using Least Square Difference (LSD) test at 5% level of probability. Data collected were also subjected to correlation and regression analysis to determine the relationship between the nutrient release, and sorption characteristics. The coefficient of determination R^2 was used to determine the model that gave the best fit of the kinetic data.

3. RESULTS AND DISCUSSION

3.1. Results of the Physical and Chemical Properties of the Soils Types

The Physical and chemical properties of the three soil types (Lixisol, Plinthosol and Acrisol) are presented in Table 1. The pH of the soils was slightly acidic and ranged between (6.6 - 6.8). Nitrogen content ranged from 0.010 to 0.017 g/kg, 0.015 to 0.019 g/kg and 0.014 to 0.018 g/kg for Lixisol, Plinthosol and Acrisol at 0 cm - 15 and 15 cm -30 cm depths respectively. Organic carbon ranged between 4.88 to 5.21 g/kg, 4.52 to 5.81 g/kg and 4.26 to 5.46 g/kg for Lixisol, Plinthosol and Acrisol at 0- 15 and 15-30 cm depths respectively. The concentrations of nitrogen, organic carbon and phosphorous was highest in Plinthosol (Table 1) compare with the other soil types. The cation exchange capacity and exchangeable acidity of the soils were low which confirms the soil to be low in fertility.

Preliminary visual inspection showed that the soils were dark grey in colour indicating a low amount of humus. It was also noted that all soils had high sand content. Reddish soil indicates the presence of iron oxides. Color is one of the characteristics of soil, which tells much about the origin of the soil and its composition (Wuana *et al,* 2010). Textural analysis showed the preponderance of sand and clay fractions thus classifying the soil as sandy clay loam soil.

Table 1: Physical and chemical properties of the soils used for the study

S/N.	Sample depth (cm)	pH	N	O.C	Av. P	Ex. A	Na	K	Ca	Mg	Sand	Silt	Clay	Extractable	Extractable
			(gkg^{-1})		($mgkg^{-1}$)	$H^+ + Al^{3+}$	($cmolkg^{-1}$)				(gkg^{-1})			Al (Mehlich)	
1	Lixisol 0-15	6.8	0.017	5.21	23.78	0.4	0.471	0.602	0.210	0.301	702	29	269	2.41	0.368
2	Lixisol 15-30	6.6	0.010	4.88	23.01	0.4	0.464	0.589	0.241	0.352	652	98	250		
3	Plinthosol 0-15	6.8	0.019	5.81	26.12	0.2	0.456	0.586	0.216	0.304	676	31	293	2.45	0.363
4	Plinthosol 15-30	6.6	0.015	4.52	24.56	0.4	0.442	0.571	0.245	0.321	750	26	224		
5	Acrisol 0-15	6.8	0.018	5.46	24.38	0.2	0.468	0.592	0.221	0.334	617	97	286	2.38	0.212
6	Acrisol 15-30	6.8	0.014	4.26	21.22	0.2	0.450	0.581	0.238	0.341	745	41	214		

Av.P Available phosphorus, Ex.A: Exchangeable acidity, Org. C: Organic Carbon, N: Nitrogen, Na: Sodium, K: Potassium, Ca: Calcium, Mg: Magnesium

Table 2: Chemical properties of the amendments

Parameters	Compost	REFB	Biochar
PH	6.59	9.45	11.03
Electrical conductivity (ds/m)	0.01	0.01	0.02
Ash content (gkg^{-1})	64.00	91.56	93.73
Nitrogen (gkg^{-1})	0.73	0.57	0.42
Organic carbon (gkg^{-1})	50.4	38.9	82.6
Phosphorus (gkg^{-1})	0.723	2.77	2.64
Potassium ($cmolkg^{-1}$)	2.84	5.76	0.74
Sodium ($cmolkg^{-1}$)	0.31	0.58	0.34
Calcium ($cmolkg^{-1}$)	0.50	0.72	0.69
Magnesium ($cmolkg^{-1}$)	0.34	0.48	0.61
Iron (gkg^{-1})	1.36	0.26	0.90
Copper ($mgkg^{-1}$)	38.23	34.47	69.12
Zinc (gkg^{-1})	0.24	0.22	0.21
Manganese (gkg^{-1})	0.40	0.16	0.33
CEC (cmol/kg)			65.58
Surface area (cm^2g^{-1}			867.95
Moisture content (%)			0.88
Volatile matter (%)			11.84
Liming value			9.53
Fixed carbon			81.30

REFB; Raw oil palm empty fruit bunch; NPKMg; Nitrogen, Phosphorus, Potassium, Magnesium (12:12: 17:2)

Although the organic carbon content of the soils was generally low; the plinthosol soil had the highest value. Rosenani and Mohd Zikri, (2006), reported that low to medium organic carbon rate for tropical soil was attributed to paucity of vegetation cover, rapid mineralization of organic matter, inadequate return of crop residue, bush burning and short fallow periods. The critical level of organic matter for optimum crop production was given as 30 g/kg (Amlinger, et al., 2007). Exchangeable bases were in the order of K > Na > Ca > Mg for all the locations and across depths.

The soils differed in their available P status and characteristics in all locations across depths which were expected to affect P retention and release. Available P was moderate thus indicating the good phosphorus fertility of the soils being above critical P level in Nigerian soils of 15mg/kg. (Enwezor *et al.,* 1990; Antelo, *et al.* 2007). The moderate phosphorus content of some tropical soils has been attributed to high apatite content of the soil forming minerals (Atiyeh, *et al.* 2000). It has also been suggested that high P content in these soils in addition to apatite content, may be due to their level of maturity. All the soil samples show medium level of available phosphorus.

Total nitrogen content was below the critical level of 1.50 g/kg for optimum crop production in Nigeria (Amlinger *et al.,* 2007). The values were irregular across depth in each of the soils. It has been documented that temperature and moisture have profound effects on Nnitrogen availability through their effect on Nnitrogen mineralization, transformation and movement (Ayeni, *et al.* 2008). Exchangeable Ccalcium is the principal saturating cation and mostly abundant in these soils across the depths and fields. The critical level of the Ccalcium ions was given as 2.6 Cmol/kg (Amlinger, *et al.* 2007). Exchangeable sodium ions of the soils increased as the depth increase, magnesium decreases as the depth increases. Potassium ions decreasees as the depth increases, having critical level for most crops of 0.20 Cmol/kg. The soils are generally low in CEC, which corroborates the results of the metals. The soil had an average cations exchange capacity (CEC) of 1.5 Cmol/kg. The CEC parameter particularly measures the ability of soils to allow for easy exchange of cations between its surface and the solution. The relatively low levels of silt, clay and average level of CEC indicate the high permeability, hence leachability of nutrients and heavy metals in the soil and suggest that it might be amenable to remediation by use of amendment materials (Ehsan *et al.* 2006; Atafar *et al.* 2010). Cations (positively charged ions) useful to plant nutrition include Mg^{2+}, Ca^{2+}, K^{+}, and Na^{+}.

3.2. Chemical Properties of the Amendments (Raw, Composted and Biochar)

The chemical composition of the amendment is presented in Table 2. The result indicated that pH was slightly acidic (6.59), to alkaline (9.45) and (11.03) for compost, raw empty fruit bunch (REFB) and biochar respectively. The electrical conductivity of compost and REFB was 0.01ds/m and 0.02 ds/m for biochar. The ash content of compost 64.00 g/kg was considered low compared with 91.56 and 93.73 g/kg for REFB and biochar. Nitrogen content of the amendment was high in compost followed by REFB and biochar. Plinthosol has highest extractable Iron (Fe) value of 2.45 mg/kg and extractable Aluminium (Al) value of 0.353 mg/kg Biochar amendment had the highest organic carbon content of 82.8 g/kg.

The results showed that organic Carbon of the amendment materials is of main importance for the formation of stable soil organic matter in soils. The compost analyzed contains significant amounts of valuable plant nutrients including N, P, K, Ca, Mg and S as well as a variety of essential trace elements (Bolland, et al. 2001; Amlinger et al., 2007). These properties have fundamental importance for a range of effects of the REFB and Bbiochar on soil properties.

The electrical conductivity of biochar was found higher than that of the compost and the REFB. From the results, there is a tendency for high amount of electrolytes to be added unto the soil which could affects its flocculation.

It has been reported that pH can be high or low depending upon feedstock and production conditions. A high pH can be a key feature of biochar in improving acid soils which is a characteristic feature of the soil supporting the oil palm. The nutritive concentration of the REFB was higher compared to that of the Ccompost and Bbiochar, with respect to Mmagnesium, Ccalcium, Ppotassium and Sodium concentrations, which influences cation exchange capacity (CEC). CEC is a measure of the surface charge in soil. CEC increases as biochar ages and this has been attributed to an increase in some of the oxygenated functional groups on the surface of the amendments. Interactions between surfaces of the amendments and soil particles, dissolved organic matter (DOM), gases and water are also a function of the total surface charge and total concentration of functional groups (Adeniyan and Ojeniyi, 2005; Braimoh and Vlek, 2006).

The results of the experiment show that pyrolyzed EFB has the highest pH value (11.03), organic carbon (83 g/kg) and highest copper concentration, implying that the biochar form of EFB is a suitable soil amendment for acid soils, soils low in soil organic carbon as well as those low in copper as an essential micronutrient (Table 2). The raw EFB has the highest concentration of potassium thereby demonstrating a good source of potassium when used as amendments in soils of low potassium concentration. This is essentially important in oil palm plantations as potassium plays a crucial role in oil palm nutrition. The composted EFB gave the highest nitrogen concentration closely followed by the raw EFB. Nitrogen is a key essential nutrient in oil palm metabolism and it is responsible for vegetable growth. The high level of nitrogen in the composted EFB provides an opportunity to improve the productivity of low-nitrogen soils.

The rate at which nutrients are released from the different forms of EFB under different conditions in different soil types is another important concern and this study made attempt to fill in the gap. It has been reported that NO_3^{-} mobility is often related to the organic matter content and could be due to the higher cation exchange capacity (Hamdi, *et al.* 2013).

3.3. Ammonium Nitrogen Release for Amended and Unamended Soils

NH_4^{+}- N release for amended and unamended soils are shown in Figures 2-6. There was a decrease in the release across depths (0-15 and 15-30 cm) throughout the duration of the study. However, Lixisol amended with NPKMg has the highest NH_4^{+}-N release (Figure 2) than the other amendments and control. Similar trend was observed at 15-30 cm depth. Lixisol amended with NPKMg showed maximum release of ammonium nitrogen (Figure 3) followed by Lixisol amended with compost. At 0-15 cm depth, Plinthosol amended with compost showed the highest release of ammonium nitrogen (Figure 3). However, at 15-30 cm depth, Plinthosol amended with NPKMg also showed the highest release (Figure 4) compared with other amendments and control. At 0-15 cm depth, Acrisol amended with REFB showed the highest release of ammonium nitrogen (Figure 5) followed by Acrisol amended with compost. At 15-30 cm depth. Acrisol amended with compost has the highest release of ammonium nitrogen (Figure 6) compared with other amendments and control.

In the present study it was observed that treatments and fertilizers had significantly increased the concentration of mineral nitrogen (NH_4^+ and NO_3^- nitrogen) in soil due to net mineralization during the study period. Evidently the amount of N released into the soil increased with increase in the weeks of observation. However, amount of release of nitrogen from treatments varied among the treatments and at different time periods. This was in agreement with the similar reports of Yadvinder, *et al.,* (1992). The results have shown in the Figures 2-6 indicated a significant increase in the NH_4^+ - N mineralization in the first two weeks, which continued to increase as the week progresses.

3.4. Nitrate – Nitrogen Release for Amended and Unamended Soils

NO_3^- - N release for amended and unamended soils under field condition is presented in Figures 7-13. The results showed that there was a gradual decrease in nitrate- nitrogen release throughout the duration of the study. However, at 0-15 cm depth, Lixisol amended with REFB has the highest nitrate - nitrogen release (Figure 7). Plinthosol amended with biochar showed the highest nitrate -nitrogen release at 0-15 cm depth (Figure 8), whereas Plinthosol amended with REFB showed the highest release (Figure 9) across depths (0-15 and 15-30 cm), Acrisol amended with compost and REFB also showed high NO_3^- - N release compared with the other amendments and control.

From the results it can be seen that the extent of interaction time required for high nitrate release of by the soil type was determined on the initial NO_3^- concentration and on organic matter and soil texture. This interaction proffer that at the onset, sorption takes place rapidly on the soil surface then by diffusion. This pattern in NO_3^- release suggests that the binding may be through interactions with functional groups located on the surface of the soil (Hamdi, *et al.* 2013). Further, our results indicate that there were considerable differences in the pattern of N release from added organic amendments during the study period due to the difference in their chemical composition and extent of mineralization. The added amendments regulated N release.

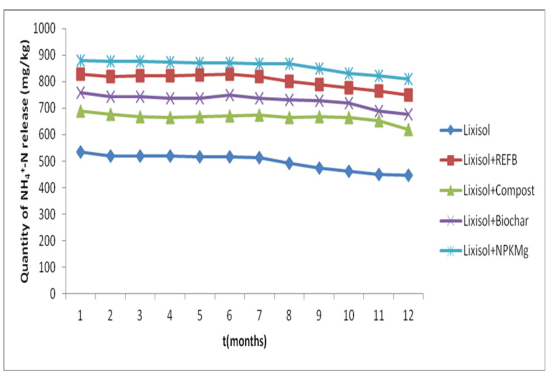

Figure 2: Ammonium -nitrogen release at (0 -15 cm) depth for Lixisol amended and unamended soils in field experiment

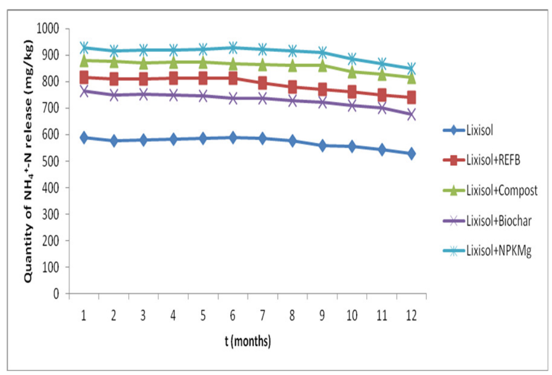

Figure 3: Ammonium -nitrogen release at (15 -30 cm) depth for lixisol amended and unamended soils in field experiment

O.M. Ekebafe et al. / Nigerian Research Journal of Engineering and Environmental Sciences
8(1) 2023 pp. 179-193

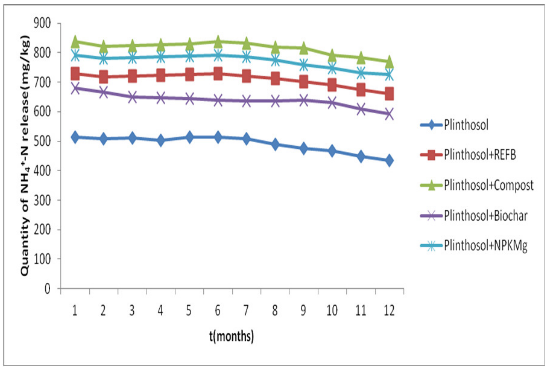

Figure 4: Ammonium -nitrogen release at (0 -15 cm) depth for Plinthosol amended and unamended soils in field experiment

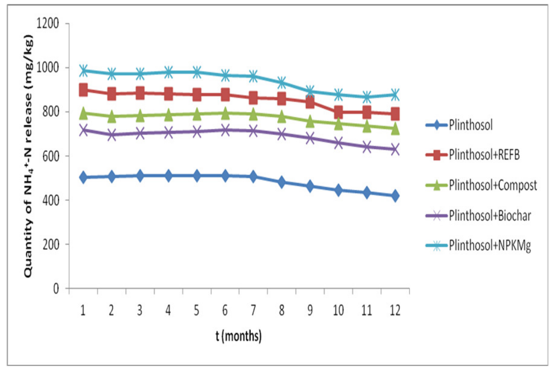

Figure 5: Ammonium-nitrogen release at (15-30 cm) depth for Plinthosol amended and unamended soils in field experiment

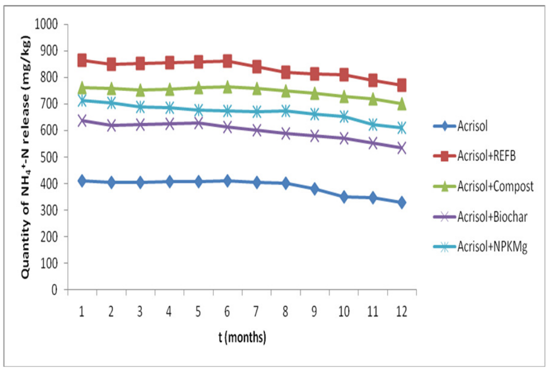

Figure 6: Ammonium-nitrogen release at (0-15 cm) depth of Acrisol amended and unamended soils in field experiment

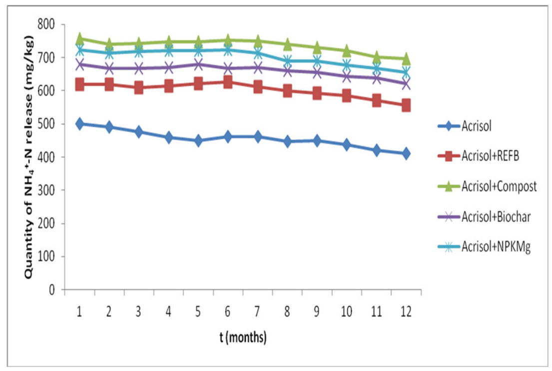

Figure 7: Ammonium-nitrogen release at (15-30 cm) depth of Acrisol amended and unamended soils in field experiment

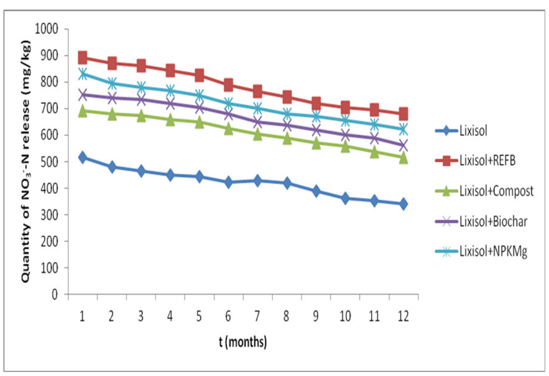

Figure 8: Nitrate-Nitrogen release at (0-15 cm) depth of Lixisol amended and unamended soils in field experiment

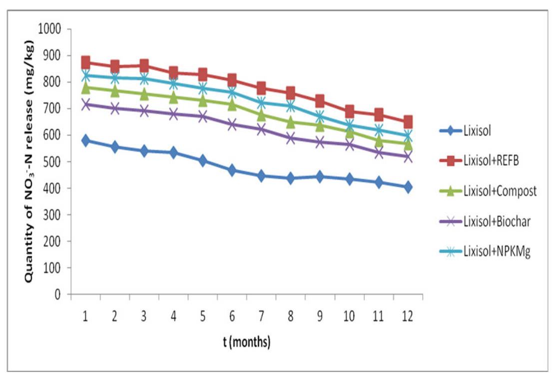

Figure 9: Nitrate-Nitrogen release at (15-30 cm) depth of Lixisol amended and unamended soils in field experiment

O.M. Ekebafe et al. / Nigerian Research Journal of Engineering and Environmental Sciences
8(1) 2023 pp. 179-193

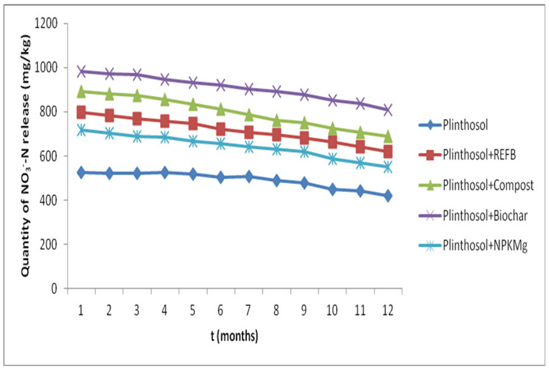

Figure 10: Nitrate-Nitrogen release at (0-15 cm) depth of Plinthosol amended and unamended soils in field experiment

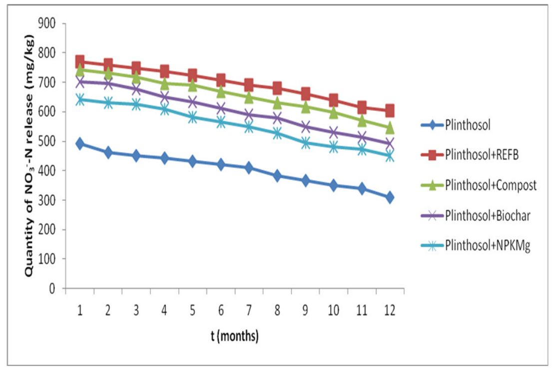

Figure 11: Nitrate-Nitrogen release at (15-30 cm) depth of Plinthosol amended and unamended soils in field experiment

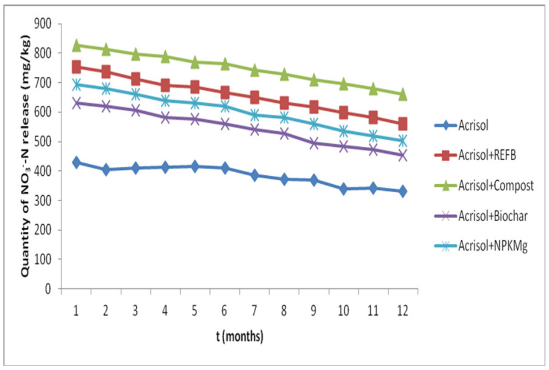

Figure 12: Nitrate-Nitrogen release at (0-15 cm) depth of Acrisol amended and unamended soils in field experiment

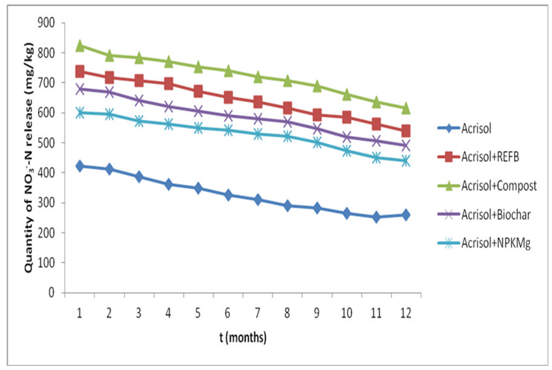

Figure 13: Nitrate-Nitrogen release at (15-30 cm) depth of Acrisol amended and unamended soils in field experiment.

3.5. Kinetic Parameters for Ammonium Nitrogen Release and Nitrate Nitrogen in Amended and Unamended Soil

The results of the NH_4^+-N release in amended and unamended soils are presented in Table 3 It was observed that the order of release was pseudo second order followed by pseudo first order and Elovich model. The results of the kinetic study of nitrate nitrogen release is show in Table 4. The Pseudo second order best fits the kinetic release. The kinetic models result shows that the nitrogen release fitted the pseudo first order, pseudo second order and the Elovich equation. The results indicated that the pseudo 2nd order fits better than the orders in terms of the correlation factor. It was observed that the R^2 value was high ($R^2 > 0.9$) for all the treatments. Odhiambo (2010) also reported similar such reports from his study on nitrogen release by green manure in different soil types. It was observed from the study that the amount of NH_4^+ - N and NO_3^- - N release significantly differed among the treatments. Under field condition, different kinetic models were used to describe $NH4^+$- N and NO_3^-N release. The kinetics for NH_4^+- N releases in the three soil types fits the three models which means that the NH_4^+- N reaction is heterogeneous, and nutrients are strongly held to the soils by chemisorptive bond (Hamdi, *et al.* 2013). Similarly, the release also signifies two adsorption sites which allow a stable binuclear bond to be formed. The release followed first order model which assumed that each release is adsorbed unto one sorption site that allowed stable mononuclear bond to be formed. Odhiambo (2010) also reported similar reports from this study on nitrogen release by green manure in different soil types. The kinetics for NO_3^-N release in all the soil types and amendments fits the pseudo second order model.

The results have shown in the Table 3 and Figures 2-7, indicated a significant increase in the NH_4^+ - N mineralization in the first two weeks, which continued to increase as the week progresses. The mineralization of nitrogen is the transformation of nitrogen from organic into inorganic form and the immobilization is the reversal of the process. These processes are biochemical in nature and are mediated through the activities of microorganisms (Laos, *et al.* 2000). The resulting effects of these two processes are expressed as net mineralization or net immobilization which decides the nitrogen supply to the growing crops.

At the same time the release pattern of nitrogen in soil is affected by soil properties (Patil and Sarkar, 1994; Jensen, *et al.* 2005). Besides, release of nitrogen in proper dose at proper time is very essential for increasing the crop productivity. Thus, understanding the process of release mode and nitrogen availability in different organic and inorganic treatments, are essential to avoid nutrient deficiency and successful crop production.

The NH_4^+, NO_3^- and total available nitrogen content of the soil depend on the balance between the factors which influence the concentration of these nutrients. The nature of materials, their release pattern and condition of soil are the three most important factors affecting the N release (Jensen, *et al.* 2005). In the present study it was observed that treatments and fertilizers had significantly increased the concentration of mineral nitrogen (NH_4^+ and NO_3^- nitrogen) in soil due to net mineralization during the incubation period. Evidently the amount of N released into the soil increased with increase in the weeks of observation. However, amount of release of nitrogen from treatments varied among the treatments and at different time periods. This was in agreement with the similar reports of Yadvinder, *et al.* (1992).

Table 3: Kinetic parameters of the models for NH_4^+- N release in amended and unamended soils for field experiment

Soil + Amendment	Pseudo first order constant			Pseudo second order constant			Elovich equation constant		
	k_1	q_e	R^2	k_2	qe	R^2	α	1/β	R^2
Lixisol (control)	0.299 (0.217)	1.144 (2.800)	0.742 (0.445)	0.0022 (0.019)	555.56 (769.23)	0.903 (0.582)	$8.61x10^{19}$ ($1.41x10^{19}$)	-16.34 (-17.01)	0.566 (0.419)
Lixisol + REFB	0.304 (0.307)	2.042 (1.130)	0.844 (0.836)	0.0750 (0.0750)	4.367 (4.386)	0.709 (0.708)	$2.32x10^{15}$ ($1.32x10^{14}$)	-26.39 (-28.70)	0.538 (0.597)
Lixisol + compost	0.289 (0.302)	2.556 (2.642)	0.589 (0.825)	0.003 (0.003)	714.29 (714.29)	0.995 (0.993)	$5.10x10^{12}$ ($2.80x10^{12}$)	-32.92 (-33.50)	0.516 (0.551)
Lixisol + biochar	0.290 (0.310)	2.094 (1.355)	0.766 (0.679)	0.003 (0.009)	735.29 (751.88)	0.994 (0.993)	$5.57x10^{15}$ ($8.90x10^{17}$)	-25.37 (-21.30)	0.494 (0.494)
Lixisol + NPKMg	0.175 (0.225)	6.457 (3.087)	0.482 (0.472)	0.003 (0.004)	751.88 (751.88)	0.993 (0.885)	$6.22x10^{17}$ ($2.78x10^{18}$)	-22.46 (-21.37)	0.406 (0.397)
Plinthosol (control)	0.350 (0.358)	1.183 (1.86)	0.795 (0.809)	0.005 (0.004)	540.54 (635.00)	0.994 (0.995)	$2.50 x 10^{13}$ ($1.74 x 10^{11}$)	-26.71 (-33.05)	0.514 (0.530)
Plinthosol + REFB	0.218 (0.188)	3.792 (4.909)	0.726 (0.407)	0.004 (0.008	751.88 (746.27)	0.995 (0.995)	$4.43 x 10^{21}$ ($2.60 x 10^{19}$)	-17.89 (-19.32)	0.490 (0.494)
Plinthosol + compost	0.183 (0.227)	4.764 (3.365)	0.361 (0.584)	0.003 (0.005)	751.88 (724.64)	0.993 (0.992)	$2.54 x 10^{12}$ ($2.82 x 10^{12}$)	-33.92 (-33.50)	0.510 (0.551)
Plinthosol + biochar	0.242 (0.172)	2.911 (6.546)	0.478 (0.430)	0.003 (0.002)	735.29 (625.00)	0.994 (0.989)	$5.51 x 10^{15}$ ($2.50 x 10^{15}$)	-25.37 (-25.30)	0.494 (0.494)
Plinthosol + NPKMg	0.242 (0.243)	2.979 (2.979)	0.631 (0.630)	0.005 (0.004)	724.64 (709.22)	0.992 (0.993)	$7.58 x 10^{17}$ ($1.20 x 10^{18}$)	-21.14 (-20.68)	0.4600 (0.440)
Acrisol (control)	0.249 (0.236)	1.843 (2.508)	0.658 (0.679	0.003 (0.003)	714.29 (714.29)	0.780 (0.780)	$6.14 x 10^{22}$ ($2.63 x 10^{18}$)	-14.46 (-18.14)	0.454 (0.377)
Acrisol + REFB	0.186 (0.186)	6.015 (4.386)	0.274 (0.567)	0.004 (0.003)	675.68 (636.94)	0.992 (0.992)	$3.22 x 10^{14}$ ($3.76 x 10^{13}$)	-25.87 (-26.04)	0.400 (0.406)
Acrisol + compost	0.186 (0.184)	4.385 (4.320)	0.567 (0.434)	0.007 (0.005)	709.22 (729.93)	0.996 (0.954)	$3.11 x 10^{21}$ ($2.26 x 10^{22}$)	-16.52 (-15.68)	0.418 (0.316)
Acrisol + biochar	0.348 (0.244)	2.818 (4.343)	0.626 (0.468)	0.003 (0.003)	617.28 (617.84)	0.989 (0.990)	$5.84 x 10^{9}$ ($6.17 x 10^{10}$)	-40.58 (-34.31)	0.555 (0.493)
Acrisol + NPKMg	0.292 (0.375)	3.518 (1.294)	0.668 (0.744)	0.003 (0.003)	625.00 (606.06)	0.994 (0.987)	$7.31 x 10^{10}$ ($6.97 x 10^{9}$)	-40.55 (-39.76)	0.522 (0.488)

The values in parenthesis () is the P release for the depth (15 – 30 cm)

During the mineralization process ammonia is first released into the soil on which the nitrification bacteria acts and oxidizes into nitrate form. More ammonium tends to accumulate if the nitrification process is inhibited on the other hand ammonium content decreases with the increase in the nitrate form (Jensen, *et al*., 2005). Under the conditions of the study, immediately after the application of the treatments, there was an increase in the concentration of NH_4^+ - N. This release of NH_4^+ - N content is attributed to the decomposition of the easily decomposable nitrogenous substances present in the treatment materials. This is in corroboration with the results of Preusch, *et al.* (2002) and Gonzalex *et al.,* (1995).

Table 4: Kinetic parameters of the models for NO_3^- - N release in amended and unamended soils for field experiment

Soil + Amendment	Pseudo first order constant			Pseudo second order constant			Elovich equation constant		
	k_1	q_e	R^2	k_2	qe	R^2	α	1/β	R^2
Lixisol (control)	0.147 (0.226)	7.261 (3.090)	0.2348 (0.4509)	0.0056 (0.0055)	540.540 (507.614)	0.9966 (0.9915)	2.39×10^{13} (2.15×10^{12})	-22.48 (-23.54)	0.5143 (0.5264)
Lixisol + REFB	0.279 (0.290)	4.227 (3.296)	0.7273 (0.7589)	0.0036 (0.0029)	666.667 (666.667)	0.9933 (0.9916)	2.79×10^{10} (3.21 x1 0^{10})	-40.15 (-38.99)	0.5596 (0.5020)
Lixisol + compost	0.265 (0.268)	10.139 (11.803)	0.9243 (0.9390)	0.0024 (0.0020)	613.50 (561.800)	0.9861 (0.9842)	7.94×10^6 (1.09×10^6)	-71.66 (-88.33)	0.8295 (0.8067)
Lixisol + biochar	0.286 (0.244)	9.015 (12.764)	0.9071 (0.9350)	0.0021 (0.0023)	568.180 (568.182)	0.9026 (0.9010)	2.09×10^6 (2.16×10^6)	-78.10 (-73.40)	0.8331 (0.8297)
Lixisol + NPKMg	0.233 (0.219)	16.218 (19.724)	0.8954 (0.9111)	0.0025 (0.0023)	609.76 (584.800)	0.9888 (0.9908)	3.36×10^6 (1.57×10^6)	-79.63 (-85.87)	0.8875 (0.8868)
Plinthosol (control)	0.263 (0.187)	3.550 (8.590)	0.5588 (0.4965)	0.0030 (0.0047)	523.560 (502.513)	0.9867 (0.9880)	7.41×10^7 (6.26×10^9)	-39.50 (-31.65)	0.5645 (0.5573)
Plinthosol + REFB	0.228 (0.246)	14.639 (11.429)	0.9185 (0.9247)	0.0024 (0.0029)	613.501 (588.240)	0.9861 (0.9866)	9.77×10^6 (1.04×10^7)	-70.30 (-67.56)	0.8603 (0.8300)
Plinthosol + compost	0.272 (0.251)	11.298 (14.757)	0.9036 (0.8570)	0.0022 (0.0017)	588.241 (526.321)	0.9908 (0.9916)	1.52×10^6 (8.75×10^5)	-85.94 (-87.64)	0.8466 (0.8719)
Plinthosol + biochar	0.211 (0.279)	19.956 (11.298)	0.9175 (0.8122)	0.0013 (0.0023)	609.760 (476.190)	0.9888 (0.9928)	3.20×10^6 (4.31×10^5)	-80.00 (-88.22)	0.8817 (0.8714)
Plinthosol + NPKMg	0.237 (0.217)	16.181 (21.878)	0.8960 (0.8978)	0.0022 (0.0021)	555.556 (454.550)	0.9870 (0.9861)	9.04×10^5 (2.44×10^5)	-90.22 (-93.25)	0.9041 (0.8905)
Acrisol (control)	0.296 (0.198)	3.491 (6.486)	0.7588 (0.3579)	0.0034 (0.0043)	505.051 (500.000)	0.9891 (0.9894)	111.625 (1.31×10^{10})	-40.21 (-30.06)	0.5831 (0.6034)
Acrisol + REFB	0.212 (0.274)	18.493 (10.789)	0.8822 (0.8843)	0.0023 (0.0022)	552.486 (500.000)	0.9916 (0.9921)	2.40×10^6 (6.84×10^5)	-74.76 (-82.89)	0.8893 (0.8567)
Acrisol + compost	0.196 (0.1865)	18.621 (25.704)	0.9717 (0.9732)	0.0023 (0.0023)	584.795 (537.634)	0.9908 (0.9920)	7.47×10^6 (5.76×10^5)	-64.86 (-86.02)	0.8594 (0.8228)
Acrisol + biochar	0.196 (0.189)	23.067 (25.351)	0.9049 (0.8631)	0.0016 (0.0025)	500.000 (609.756)	0.9527 (0.9888)	1.08×10^6 (7.09×10^5)	-77.77 (-78.79)	0.8906 (0.9129)
Acrisol + NPKMg	0.207 (0.263)	22.751 (12.087)	0.9293 (0.8890)	0.0022 (0.0020)	555.556 (436.680)	0.9870 (0.9788)	5.05×10^5 (4.31×10^5)	-86.96 (-84.06)	0.8909 (0.8513)

The values in parenthesis () is the P release for the depth (15 – 30 cm)

This process is brought about by microorganisms present under various soil and climatic conditions and also under anaerobic conditions (Moazed *et al.* 2010). Whereas the decrease in NH_4^+ - N than control as observed in some of the treatments (lixisol + NPKMg, plinthosol + NPKMg, and acrisol + NPKMg) indicated the utilization of NH_4^+ by soil microorganisms or by volatilization losses (Recous, *et al.* 1995). Also, nitrification brings about a decrease in the concentration of NH_4 $^+$ - N. Similarly increase in the concentration of NO_3^- - N was observed in several treatments after the incubation as a result of the activity of nitrifying bacteria which converts NH_4^+ - N into NO_3- N. As a result of release in NH_4^+ - N or NO_3^- - N or both the total available nitrogen has increased.

The kinetic models result shows that the nitrogen release fitted the pseudo first order, pseudo second order and the Elovich equation. The results indicated that the pseudo 2nd order fits better than the orders in terms of the correlation factor. It was observed that the R^2 value was high ($R^2 > 0.9$) for all the treatments. Odhiambo (2010) also reported similar such reports from his study on nitrogen release by green manure in different soil types. It was observed from the study that the amount of NH_4^+ - N and NO_3^- - N release significantly differed among the treatments. Linear regression analyses were performed to correlate properties of all the soils studied with the NO_3^- - N release pattern. The results demonstrate that the positively correlated with the pseudo first and pseudo second order better than the Elovich equation.

Previous studies have documented analogous correlations between NO_3^- - N as those documented in this study. Several studies have shown those higher soil clay content results in increased surface area and a greater number of sorption and release sites; thus, soils with less clay content typically release more micronutrients more readily than clay soils (McDowell *et al.,* 2001; Penn *et al.,* 2002; Sims and Pierzynski, 2005; Zhang *et al.,* 2005).

The soils of acrisol are coarser in texture and are not capable of holding N in clay lattice for greater period. Thus, acrisol soils behaved better in terms of release of mineral N at different incubation times with added amendments. Haer and Benbi (2003) also observed that organic carbon and clay content could account for 91 percent variability in N mineralization of soils. Similarly, Gupta *et al.,* (2003) and Sathya *et al.,* (2009) reported that higher mineralization occurs in fine texture soils (more in clay loam than sandy loam) at different periods of incubation possibly due to the exposure of physically protected organic matter during grinding and fine sieving of the soils prior to incubation. In addition, Hassink (1992) and Paul (2014) reported that in fine texture soils, a large part of organic matter present in the small pores cannot be reached by microorganisms and therefore, remain physically protected against decomposition. However, our results were in contrast to the findings of Thomsen *et al.* (2001) and Khalil *et al.* (2005) who reported that low content of clay can stimulate N release in the soils due to sorption of the decomposition substrate onto mineral particles and incorporation into soil aggregates. Srinivas *et al.* (2006) suggested that microbiologically active soils in combination with C: N ratio of the added organic material mainly regulates the N release process in the amended soils. Both amendments and time interval had significant effect on the net release of N in the soils. Yanni *et al.* (2011) also found N content to be the most important parameter determining ammonium – nitrogen release. It was also found that the pseudo first, pseudo second and Elovich model based on their correlation of determination fitted the data well as also reported by Johnson *et al.* (2007). The k values demonstrated a positive correlation with N content and release.

4. CONCLUSION

It has been shown that raw oil palm empty fruit bunch, compost and biochar were successfully prepared and characterized with significant N nutrient levels which improve the nutrients of the soils. The biochar gave the highest pH value of 11.03, ash content of 82. 6. While REFB has the highest potassium content of 0.74 cmol/kg and Compost with the highest value of 5.04 g/kg for nitrogen content. From the sorption study, that three soil that were amended showed high sorption efficiency compared to the unamended soils.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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