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Application of Laboratory-Synthesized Ammonium Zeolite LTX as Soil Amendment Additive

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Abstract

The production of ammonium-exchanged zeolite X (NH_4-LTX) and its soil amendment activity is presented. The ammonium-exchanged zeolite X was characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, particle size analysis and Fourier transformed infrared (FTIR) spectroscopy. The addition of NH_4-LTX increased the pH, total nitrogen, potassium and sodium content and water retention capacity of the soil. Consequently, the fresh weight, dry weights, plant heights, stem thickness, stem length, number of leaves, leaves areas was remarkably greater for both maize and okro planted in soils containing NH_4-LTX compared to plants in soil without NH_4-LTX.

Keywords: Synthesis; characterization; Zeolite X; ammonium-zeolite X; plant growth.

1. Introduction

Arable lands such as that of Wassa community in Ghana have little nutrient content and are highly acidic due to mining activity in the area making them unfavourable for crop cultivation. In an attempt to ameliorate the above problem, zeolite mineral was applied to contaminated soil obtained from the Wassa community. Zeolites are inorganic porous materials having a highly regular structure of pores and chambers that allow molecules to pass through and cause others to be either excluded or broken down [1, 2, 3]. They are characterized by a microporous, crystalline structure consisting of a three-dimensional framework of SiO_4 tetrahedra where all four-corner oxygen ions of each tetrahedra are shared with adjacent tetrahedral [2, 4].

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Some of the quadrivalent silicon is replaced by trivalent aluminum, giving rise to a deficiency in positive charge [2, 4, 5]. This charge deficiency is balanced by the presence of mono and divalent cations located in the pores. The high ion-exchange and retention ability of zeolites as wells as their large adsorptive affinity for water has contributed to their successful applications in soil amendment [1, 4]. Zeolite as soil amendments was also found to restore appropriate soil conditions for plant growth by balancing pH, adding organic matter, restoring soil microbial activity, increasing moisture retention, and reducing compaction [6, 7].

Zeolites have a pronounced selectivity for cations, such as ammonium and potassium, couple with the high retention ability help to retain nutrients in the root zone to be used by plants when required [8]. The porous structure of zeolite helps keep the soil aerated and moist as well as active for a long time [9]. Zeolites have been tested for use as a soil amendment on various crops, including vegetables and in greenhouses in Russia, field crops in Japan, as constituents of golf course greens and tees in order to improve drainage and aeration, to improve compaction resistance, and reduce leaching of pesticides and fertilizers from the soil [10]. Such properties distinguish zeolites as a unique material and are important in its application. For many applications, like controlled release fertilizers, most zeolites will suffice [11, 12]. Zeolite X has a wide range of industrial applications primarily due to the excellent stability of the crystal structure and the large available pore volume and surface area [13, 15].

Although the application of zeolite X is vast, little or none of its application to soil is known to date in Ghana. Hence, in this work the effect of ammonium exchanged zeolite X on soil and on the vegetative properties of two plants, maize (*Zea mays*) and okro (*Hibiscus esculentus*) was monitored. In effect, plants were harvested at weekly intervals from the date of germination to maintain constant growth cycle for comparing the effects of ammonium exchange zeolite X.

2. Materials and methods

2.1 Reagents

Distilled water was supplied by the Water Research group, KNUST. Sodium hydroxide, potassium hydroxide, aluminum oxide and sodium silicate were purchased from AnalaR Nomapur, Netherlands. Zeolite X was produced at the Water Research laboratory, KNUST.

2.2 Soil sample collection and preparation

The experiment was performed on contaminated soil obtained from Wassa, a mining area in the Western Region of Ghana. The soil sample was air-dried, grounded and sieved through a 2 mm mesh after which standard laboratory methods were use to determine the chemical properties of the soil. Different portions of zeolite ranging from 1 to 15 g/100 g soil (1, 3, 5, 7, 9 and 15 g/100 g) were added to contaminated soil samples to determine the effect of zeolite on the pH of the soil. The 5 g/100 g zeolite rate was adopted because based on several laboratory trials; it gave a better mixture and a pH of 6.3. It must be noted that most food crops grow well in the pH range of 5.0 – 7.0 as reported by Beck et al. [32]. EcoMeT P 25 pH meter was used for pH measurements between 0.00 and 14.00 with a resolution 0.01. The soil organic carbon was determined by the modified Walkley-Black method as described by Nelson and Sommers (1982). Total nitrogen was determined by the Kjeldahl digestion and distillation procedure as described in Soil Laboratory Staff (1984). The readily acid-soluble forms of phosphorus were extracted with a HCl: NH_4F mixture called the Bray's no.1 extract. Phosphorus in the extract was determined on a spectrophotometer by the blue ammonium molybdate method with ascorbic acid as reducing agent. Available potassium extracted using the Bray's no. 1 solution was determined directly using the Gallenkamp flame analyzer. Available potassium concentration was determined from the standard curve. Exchangeable bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) in the soil were determined in 1.0 N ammonium acetate (NH_4OAc) extract; Ca^{2+} and Mg^{2+} were determine complexometrically, K^+ and Na^+ were determine by flame photometry at wavelengths of 766.5 and 589.0 nm respectively. Exchangeable acidity is defined as the sum of Al + H and this was determined in 1.0 M KCl extract as described by Page et al. (1982). Effective cation exchange capacity was determined by the sum of exchangeable bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and exchangeable acidity ($Al^{3+} + H^+$).

2.3 Synthesis of zeolite X

Zeolite X was synthesized according to the method given by Kwakye-Awuah et al. [5] with some modifications The batch composition for the synthesis is given by:

5.5 Na_2O:1.65K_2O:Al_2O_3: 2.2 SiO_2: 120 H_2O

Firstly, 22.37 g of sodium aluminate powder was dissolved in 30 ml of distilled water while stir-ring until a homogeneous solution was obtained. In a separate vessel, 31.09 g of sodium hydroxide was added to 70 g of distilled water while stirring until a homogeneous solution was obtained. The sodium aluminate suspension was added to the sodium hydroxide solution and stirring was continued until a homogeneous solution was obtained. The homogeneous solution was added into a vessel containing a mixture of 71.8 g of distilled water and 46.0 g sodium silicate solution while stirring. Stirring continued until a uniform mixture was obtained. To crystallize, the solution was poured into Teflon jars and placed in an incubator for three hours at 70 °C. The solution was then heated between 93 to 100 °C in an electric oven for 2 hours. The reaction in the Teflon jars was quenched and allowed to cool to room temperature. The reaction mixture was diluted with distilled water and filtered using a Buchner vacuum 32 funnel and Whatman No 1 filter paper. The powdered samples obtained were washed copiously with distilled water. Following overnight drying of the powdered zeolite at 80 ^oC in an electrical oven, the zeolite was crushed into uniform powder with pestle and mortar, sieved and stored in a cupboard.

2.4 Preparation of Ammonium-loaded zeolite X (NH_4-LTX)

Ammonium ions were loaded into the zeolite framework by ion exchange. 50 ml of ammonium hydroxide solution at a concentration of 1 M was added to 150.0 g of zeolite X. The mixing was performed in plastic bottles placed in a conventional rotation drum for five hours. The slurry was filtered, washed copiously with distilled water, dried at 40 ºC in an electric oven and crushed. This process was repeated for three more times to obtain significant ion exchange.

2.5 Characterization of zeolite X and ammonium loaded zeolite X

Spectroscopic and microscopic analyses were used to characterize the zeolites. X-ray Diffraction (XRD), patterns of LTX and NLTX samples were recorded on a Philips PW1710 X-ray powder diffractometer over 2Ө range of 5° to 55° at a scanning speed of 2° per minute and a step size of 0.05°. The instrument uses sealed Xenon detector. The diffractometer was equipped with graphite monochromated Cu radiation source (8978 eV or l = 1.5418 Å). The X-ray source was operated at 40 mA and 40 kV. Data processing was carried out using Philips APD software with a search/match facility and an ICDD database on a DEC Microvax minicomputer interfaced to the diffractometer. Chemical compositions of LTX and NLTX in the form of oxides were analyzed by Energy Dispersive X-ray Analysis (EDS Oxford Instrument ED 2000) with an array of 16 anodes analyzing crystals and Rh X-ray tube as a target with a vacuum medium.

The structure features of LTX and NH_4-LTX were investigated with a Mattson FTIR spectrometer (Mattson Instruments, UK) equipped with a ZnSe crystal plate attached to the spectrometer with a mercury cadmium telluride A (MCTA) detector and KBr as beam splitter. Measurements were done using 100 scans at 4 cm^{-1} resolution, units of log (1/R) (absorbance), over the mid-IR region of 1200-400 cm^{-1}. Crystallite size and morphology of LTX and NLTX were studied by Scanning Electron Microscopy (JEOL JSM-6400) with applied potential 10 - 20 kV. Thermal stabilities of LTX and NLTX were investigated by TGA on a Mettler Toledo TG50 thermobalance in the temperature range of 25– 700 °C, with a heating rate of 10 °C min^{-1} under flowing air. Mass losses were determined by employing TGA curves. The second derivative differential thermal curve was used for peak temperature determinations.

2.6 Pot plant trials

Viable seeds of two plant species, namely, maize (*Zea mays*) and okro (*Hibiscus esculentus*) obtained from the Food and Agriculture Organization, Ghana (FAO), were used for the pot experiment. These individual plant species can easily be replicated facilitating statistical analysis of plant growth. 32 pots were filled with a soil- NH_4-LTX mixture (95:5 weight/weight) of which 16 was planted with maize and the rest planted with okro. Of the 32 pots with untreated soil, 16 were planted with maize with the remaining 16 planted with okro. In each case, one seed per pot was sowed. There were 64 units in all. Normal cultural practices for raising a successful crop were applied uniformly to all the 64 experimental units. The pots were irrigated at regular intervals with distilled water in order to maintained humidity suitable for plant growth. Basic plant measurements data were recorded on alternate week to evaluate the development phases of growth and development of the plants as described by.

3 Results

3.1 Results from the synthesis and characterization of zeolite X

Zeolite X was successfully synthesized in the laboratory under the conditions described above and loaded with ammonium ions by ion exchange. SEM photographs of zeolite X with and without ammonium ions are presented in Figure 1. The SEM micrograph confirmed the phase purity of the crystal morphology and also showed that the particles were closely similar in size and appearance, which suggests that the loading of ammonium ions into the framework seems to have little or no effect on the size of the zeolite.

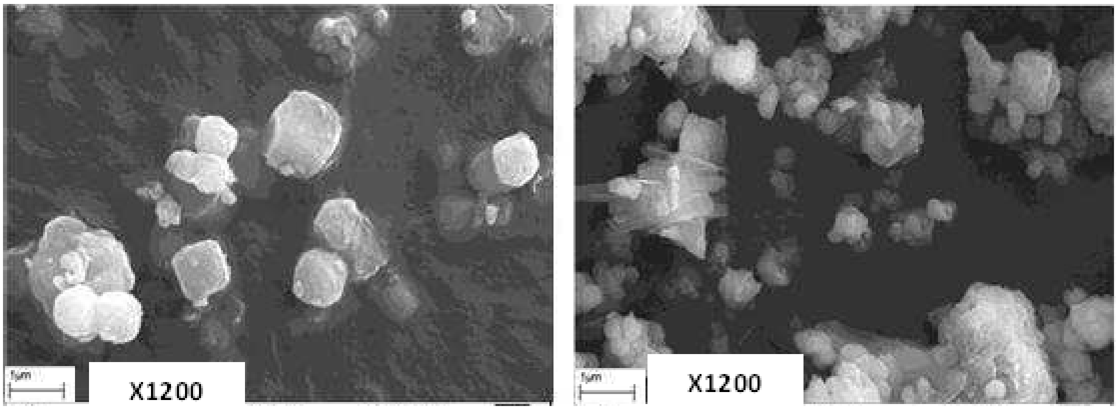

Fig.1. Scanning electron micrograph of left: zeolite X and right: ammonium-zeolite X

EDX spectrum detected ammonium ions in the zeolite framework were not detected (Figure 2). The elements used in the synthesis of other elements such as N and H (not shown) accounted for 2.37 % of the composition as determined.

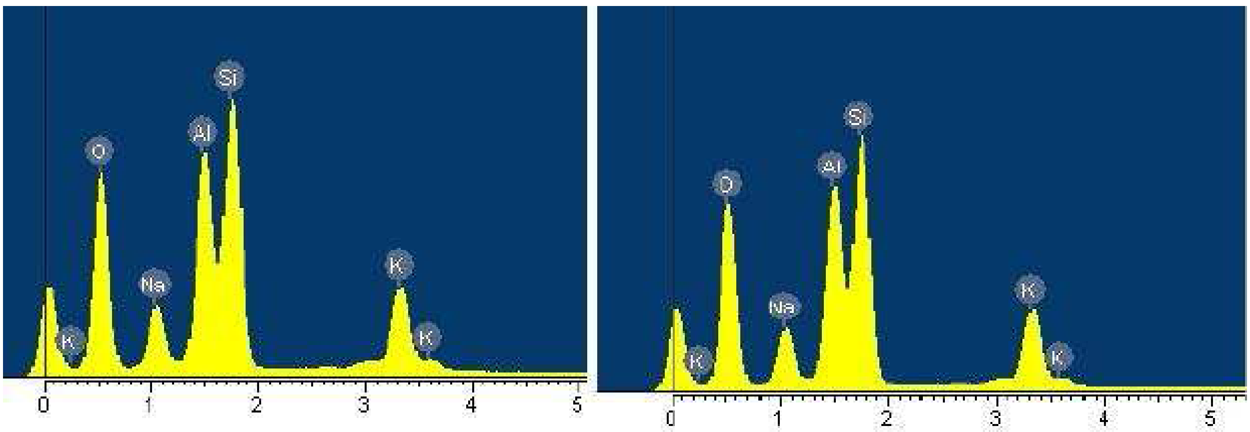

Fig. 2. EDX of zeolite X (left) and ammonium-exchanged zeolite X (right)

The mid-FTIR spectrum of the as-synthesized zeolite X is given in Figure 3 in the region of lattice vibrations (1200 – 400 cm^{-1}). A large broad band was observed in the 977 cm^{-1} in both samples. This band can be attributed to the overlap of the asymmetric vibrations of Si – O (bridging) and Si – O (non-bridging) bonds.

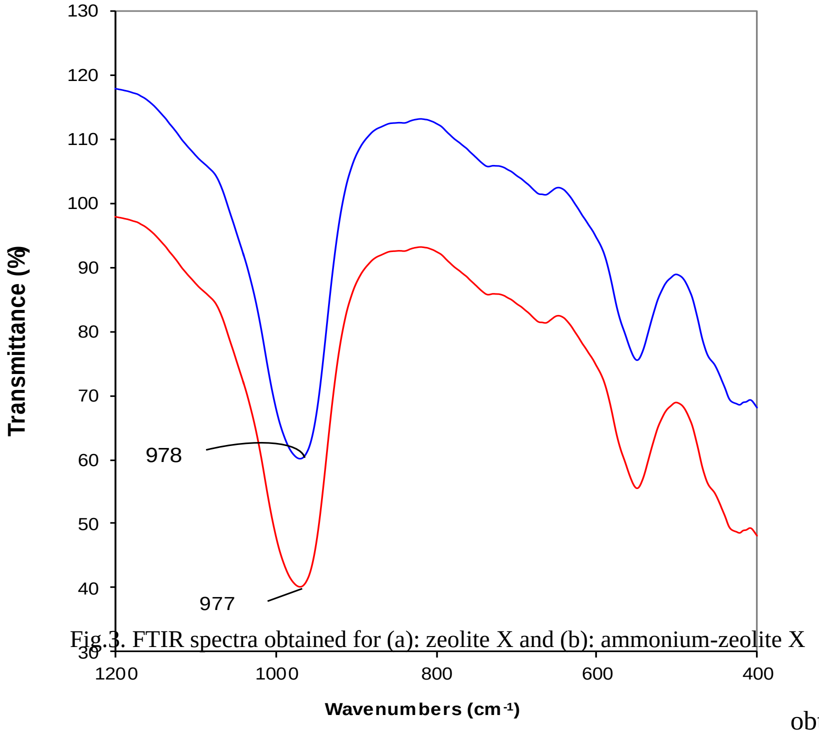

Fig.3. FTIR spectra obtained for (a): zeolite X and (b): ammonium-zeolite X

The band obtained for zeolite A with and without ammonium are presented in Figure 4. The peaks show that the particles were highly crystalline. Loading of ammonium ions did not alter the crystalline of the crystals as well as the crystallographic structure. The spectra also showed that impurities were nearly absent in the crystal lattice of the particles.

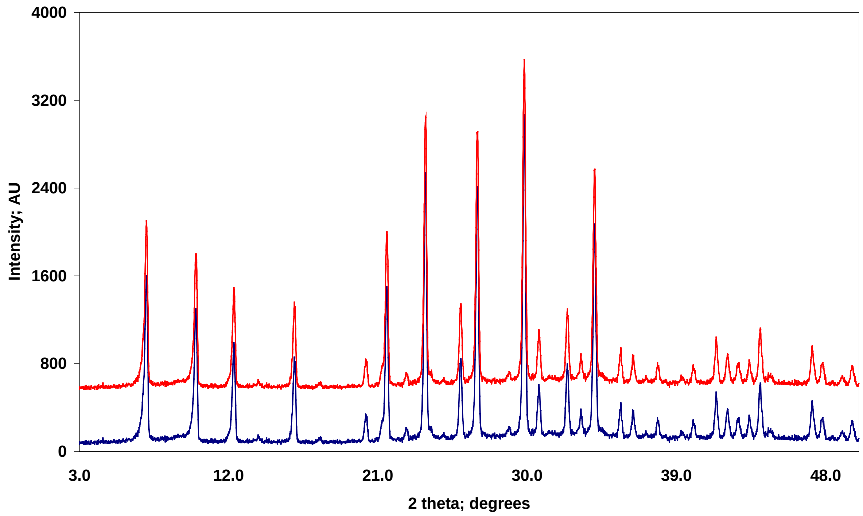

Fig.3. XRD spectra obtained for (a): zeolite X and (b): ammonium-zeolite X

Chemical properties of the soil before and after the addition of ammonium exchanged zeolite A is given in Table 2. Addition of NH_4-LTX increased the pH of the soil from 3.8 to 6.3 and total nitrogen from 0.04 to 0.33 % whilst organic carbon and organic manure remained unchanged. The concentrations of sodium and potassium increased from 0.06 and 0.04 to 0.76 and 2.71 respectively after addition of NH_4-LTX (Table 3). However, that of magnesium and calcium was unaltered. Available Bray's (Table 4) phosphorus and potassium were 0.16 and 26.78 ppm before addition of NH_4-LTX and 14.54 and 544.39 ppm respectively after addition of NH_4-LTX.

Table 2. Chemical properties of Wassa land used for the investigation

Properties	**Before amendment**	**After amendment**
pH 1:1 (H_2O)	3.80	6.30
Organic C (%)	0.45	0.45
Total N (%)	0.04	0.33
Organic M (%)	0.78	0.78

Table 3. Exchangeable cations present in the soil sample before and after addition of NH_4-LTX

Exchangeable cations	**Before amendment (meq/100g)**	**After amendment (meq/100g)**
Ca	0.80	0.80
Mg	0.27	0.27
K	0.04	2.71
Na	0.06	0.76
T.E.B.	1.17	4.54
Exch A (Al +H)	1.70	0.40
E.C.E.C.	2.87	4.95
Base salt (%)	40.77	91.90

Table 4. Available Bray's profile of the soil sample obtained before and after addition of NH_4-LTX

Available-Bray's	before amendment	after amendment
ppm P	0.16	14.54
Ppm K	26.78	544.39

3.3 Results from pot plant trials

Plant growth appeared to be markedly influenced by application of ammonium exchanged zeolite A as observed from the better plant fresh (wet) weight, dry weight, number of leaves per plant, stem thickness, stem (plant) length and leaf area compared to the same parameters in plants grown in soil without ammonium exchanged zeolite A. Data obtained were analyzed using analysis of variance and means separated using the Least Significant Difference test at 95 % confidence interval level [14]. Results obtained for maize and okro plants in height are shown in Figure 6. Plant height is an important morphological character that acts as a potent indicator for availability of growth resources in its vicinity [16]. Maize plant height increased progressively in all treatments over time. However, there was significant difference (P = 0.000, N = 2) between the number of leaves of maize plants for both treatments. There was significant difference between the samples treated with NH_4-LTX + Soil and samples with no NH_4-LTX (P = 0.000, N = 2) as well as between samples of the same treatments (P = 0.000, N = 2) as observed in the okro plants.

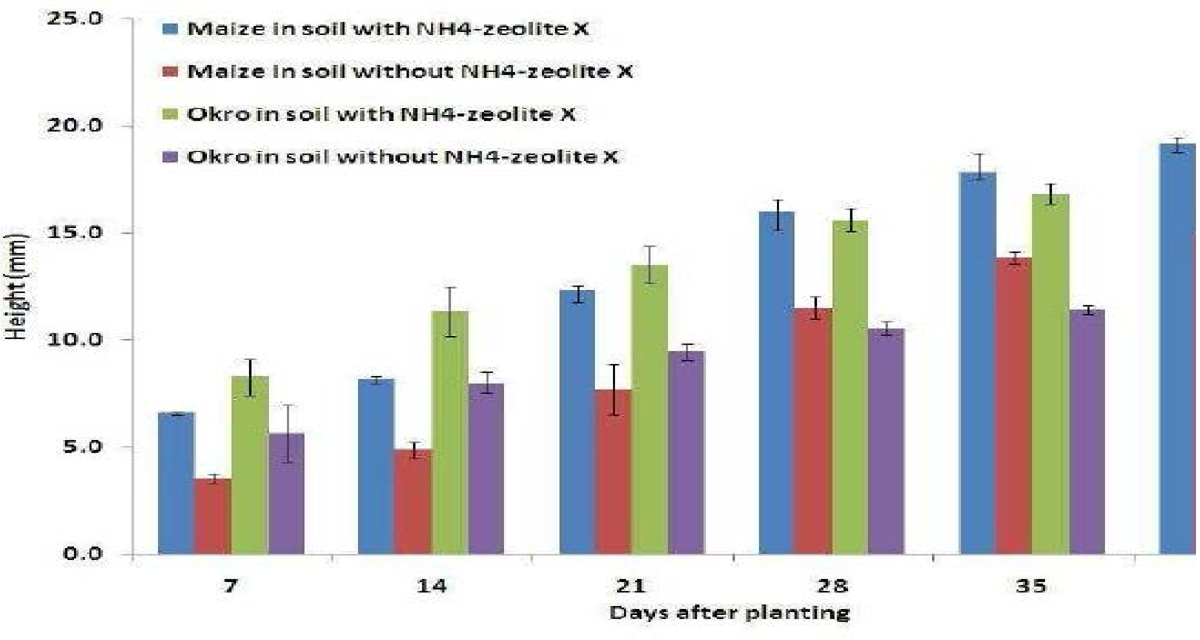

Fig. 6. Results obtained for plant height for soil with and without ammonium zeolite X for maize and okro

The number of leaves was determined by counting. The average number of leaves per okro plant, for three plants counted per treatment at six occasions during the trial, is shown in Figure 7. There was no significant difference between plants of the same treatments for example plants grown in soil without NLTX had statistical values of *P* = 0.001 and *N* = 2. However, there was significant difference between plants grown in soil + NLTX (*P* = 0.000, *N* = 2).

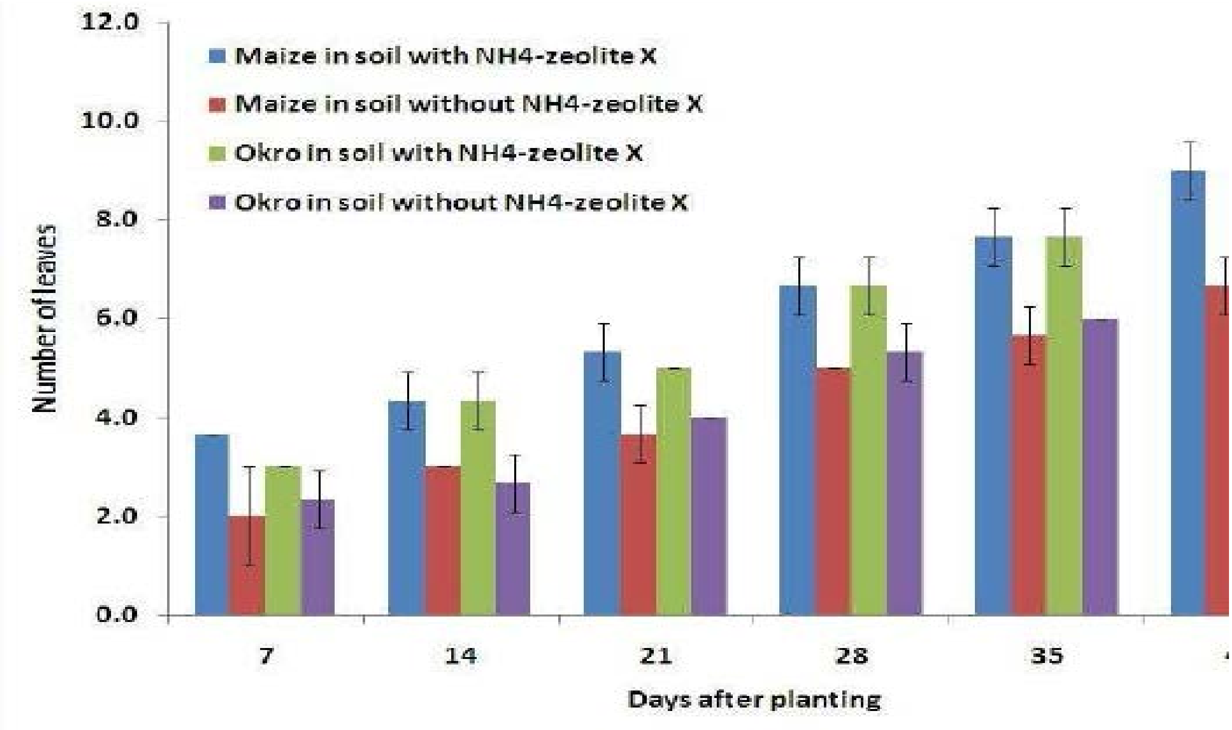

Fig. 7. Number of leaves obtained for maize and okro for soil with and without ammonium zeolite X

Figure 7 shows that the NLTX + Soil treatment develop faster during the whole trial. The NLTX + Soil treatment had the most rapid development of leaves during the whole trial. At the end, these plants had in average 8 to 10 leaves. The Soil only treatment had a clearly slower development and had in average 6 to 8 leaves at the end of the trail. There was no significant difference within samples of the same treatment (*P* = 0.181, *N* = 2). However, there was significant difference between samples of different samples (*N* = 0.000, *P* = 2). The LTX + soil treatment clearly have the highest fresh weight of approximately 6.4 g at 42 days after planting (DAP) as compared to approximately 3.8 g at 42 DAP for the soil only treatment as illustrated in Figure 8.

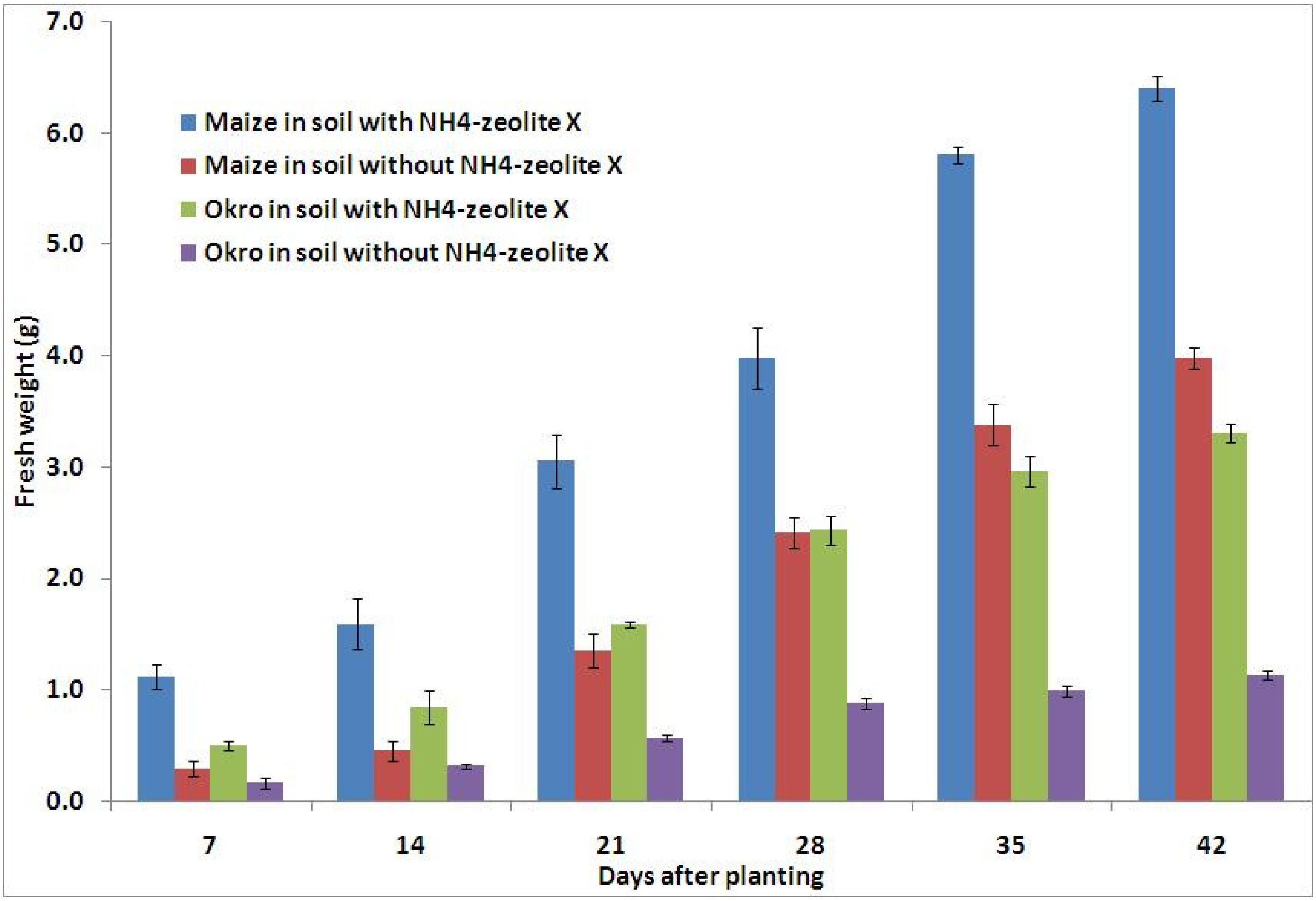

Fig. 8. Fresh weight obtained for maize and okro for soil with and without ammonium zeolite X

There was significant difference between the samples treated with NH_4-LTX + Soil and samples with no NH_4-LTX (P = 0.000, N = 2) as well as between samples of the same treatments (P = 0.000, N = 2). The dry weight of the maize and okro plants is presented in Figure 9. For maize, LTX + Soil treatment gave high values during the entire investigate period. Values obtained from the Soil only treatment were lower than that of LTX + Soil treatment. However, there was significant difference between and within treatments (P = 0.000, N = 2) throughout the investigative period. The dramatic growth behavior is thought to be due to the release of ammonium ions from the NH_4-LTX. There was significant difference between the samples treated with NH_4-LTX + Soil and samples with no NH_4-LTX (P = 0.000, N = 2) as well as between samples of the same treatments (P = 0.000, N = 2) for okro.

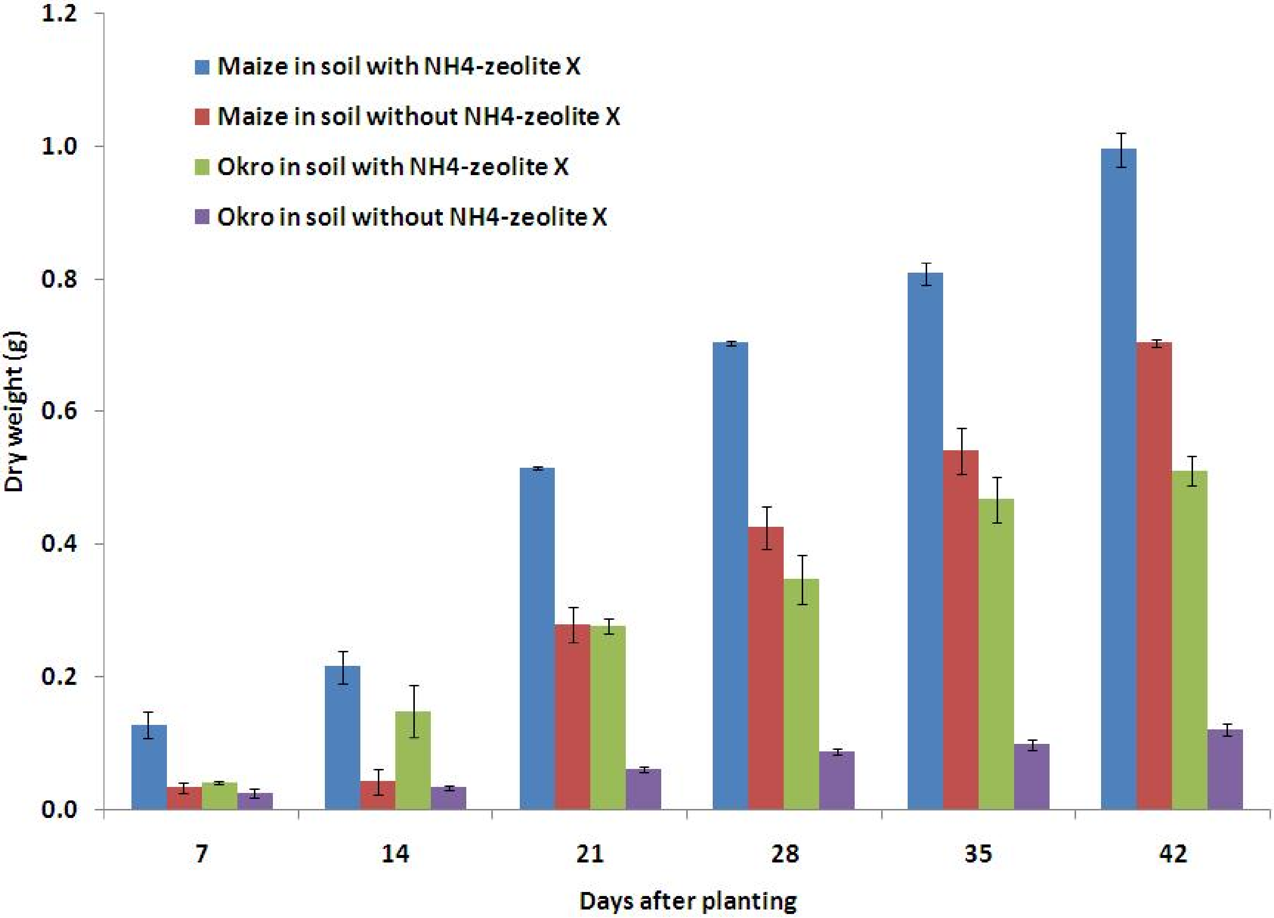

Fig. 9. Dry weight obtained for maize and okro for soil with and without ammonium zeolite X

The leaf area of the maize and okro plants is presented in Figure 10. There was significant difference (P = 0.00, N = 2) between plants of different treatments, but no significant difference within treatments (P = 0.014, N = 2). There was an observable increase in the area of the leaf from 7 DAP to the end of the experiment at 42 DAP. The largest area is measured in the LTA + Soil treatment with about 434 mm^2 at 42 DAP with the least in the Soil only treatment with a value of 58 at 7 DAP. Plants in the Soil only treatment produced values that lag that registered by the LTA + Soil treatment. There was significant difference between the samples treated with NH_4-LTA + Soil and samples with no NH_4-LTA (P = 0.000, N = 2) as well as between samples of the same treatments (P = 0.000, N = 2). This may be due to the positive effect of NH_4-LTA on cell division and cell elongation leading to enhanced leaf expansion. There was significant difference between the samples treated with NH_4-LTA + Soil and samples with no NH_4-LTA (P = 0.000, N = 2) as well as between samples of the same treatments (P = 0.000, N = 2).There was no significant difference within samples of the same treatment (P = 0.694, N = 2). However, there was significant difference between samples of different samples 63 (P = 0.000, N = 2). Soil recorded the highest values of stem thickness (Figure 11) throughout the investigative period.

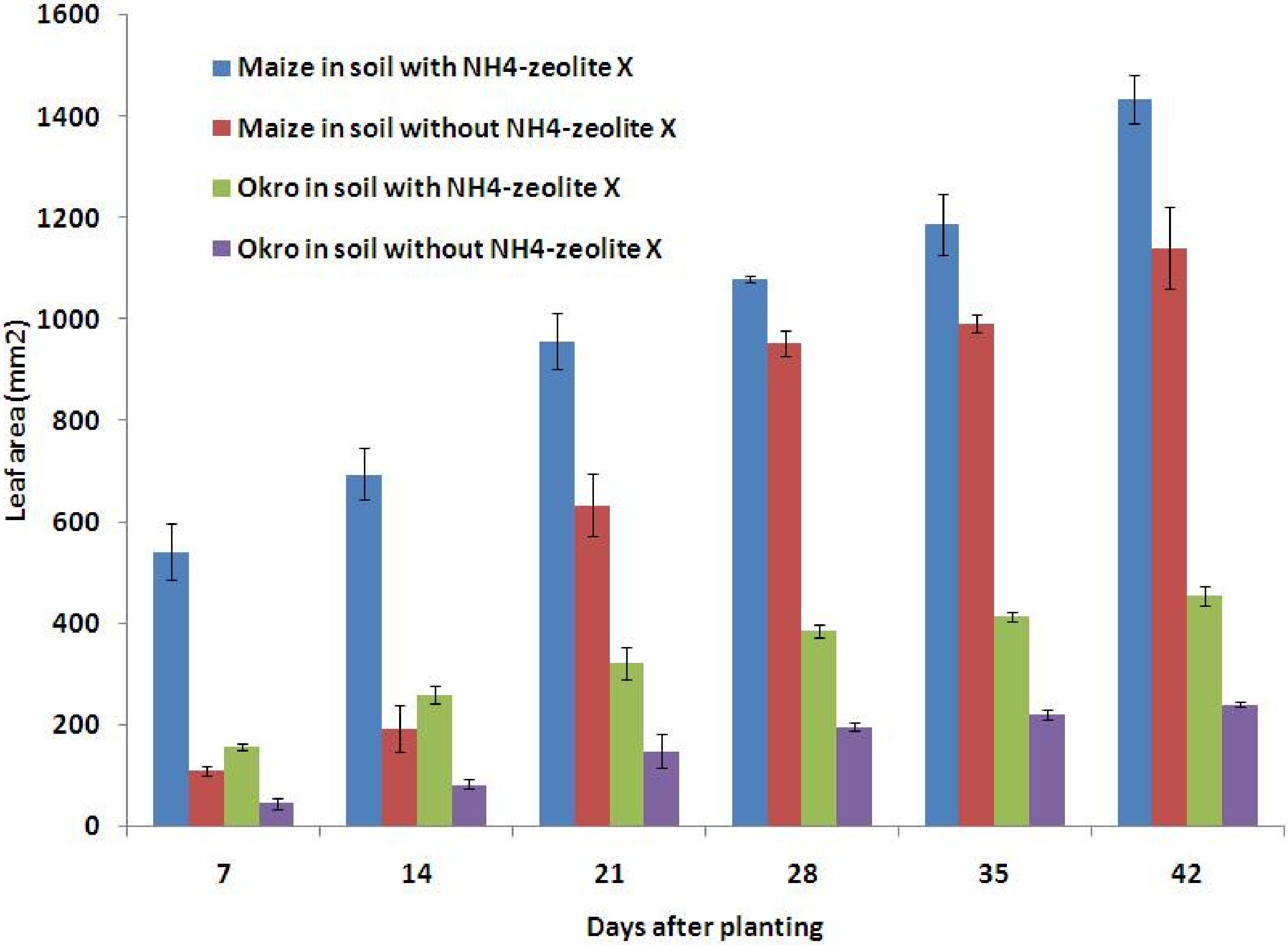

Fig. 10. Leaf area obtained for maize and okro for soil with and without ammonium zeolite X

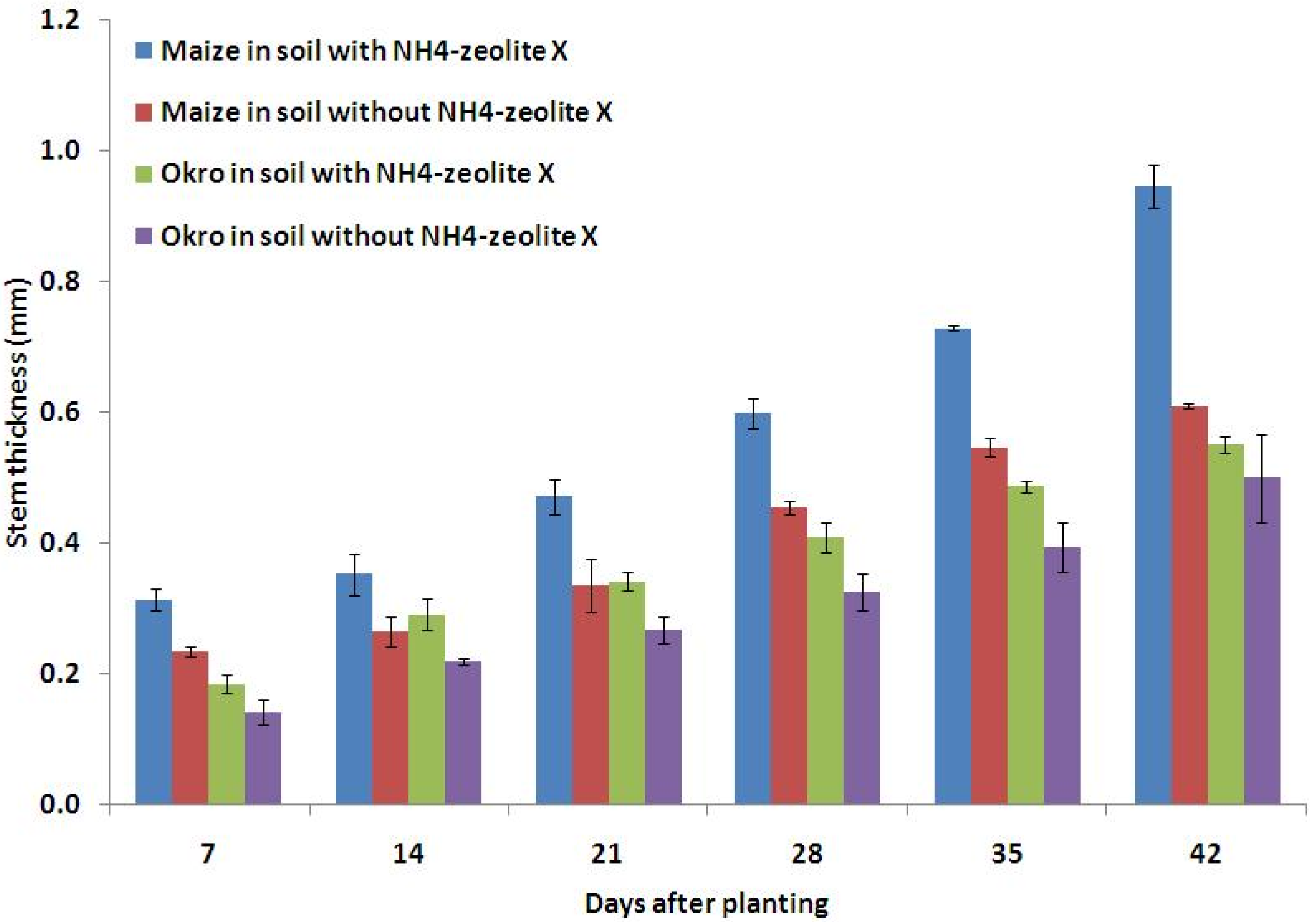

Fig. 11. Stem thickness obtained for maize and okro for soil with and without ammonium zeolite X

4 Discussions

Pre-treatment analyses showed the soil was slightly fertile and most of the nutrient elements were present in amounts close to the critical level (Table 1). Most crops grow best if the soil pH is between 5.5 and 7.5 [17]. On application of the ammonium exchanged zeolite X to the soil, the pH increased from 3.8 to 6.3.Apart from environmental factors like light, temperature and water, biomass production and healthy plant development is highly dependent on the quality and amount of nutrients applied [18]. The amount of nitrogen was found to be in the deficiency range for maize and okro [19]. The total nitrogen which is a measure of N in all organic and inorganic forms increased from 0.04 to 0.33 on the application of ammonium loaded zeolite X. This can be attributed to the ammonium loaded into the zeolite X making more ammonium available from zeolite in the plant-soil interactions during plant growth [20, 21, 22].Zeolites are known to be slow release fertilizers [23]. The higher number of leaves formed in zeolite treated plants may be due to slow-release fertilizers and its availability to plants [24]. Plant growth depends on adequate formation of leaf area for efficient interception of light [16]. Leaf areas of plants increased after emergence with the highest value at 42 DAP. Zeolite levels significantly influenced leaf area development [16, 18]. Leaf area responded positively to zeolite application. The zeolite treatment maintained higher leaf area through the experimental growth period. Plants grown with zero zeolite application gave the lowest leaf area. Enhanced leaf area development with zeolite was also reported for horticultural crops [25]. Kavoosi [24] concluded that zeolite uptake increased nucleic acid, amides and amino acid and hence cell multiplication, which increased leaf area. In this study increase in leaf area may be due to the application of NH_4-LTX which in effect increased the presence of nitrogen, which is a constituent of chlorophyll molecule and amino acids, which enhances cell multiplication and cell elongation and ultimately resulting in more leaf growth and area. Similar results were obtained by Singh and Rajodia [26].Plant height is an important morphological character that acts as a potent indicator for availability of growth resources in its vicinity. The height of a plant depends on nutrients especially on nitrogen [27]. Irrespective of zeolite application, plant height increased over time [16]. Plant height increased progressively and attaining its maximum highest at 42 DAP. This trend was similar with the result reported for pea [24, 28], for mung bean [26 – 29] and for edible oil pea [27].Although the unamended soil contain on average a little less total nitrogen of 0.04 % (from soil analysis), it is thought that the dramatic growth enhancement of plants growing in the amended substrates demonstrates an abundance of available nitrogen (0.33 %) [20]. Similar results wereobtained by Leggo et al., [30 – 32]. Basically, plant fresh weight is a genetically controlled character, but several studies have indicated that the plant fresh weight can be increased or decreased by the application of plant growth regulators [26, 27]. It was observed that there was a substantial improvement in fresh weight due to the application of NH_4-LTX. The LTX + Soil treatment gave high values during the entire investigate period for dry weight. Values obtained for dry weight from the Soil only treatment were lower than that of LTX + Soil treatment. This can be attributed to greater degree of mineralization of the soil pore-water which increases the availability of plant nutrients [26]. The dramatic growth behavior is thought to be due to the release of ammonium ions from the ammonium-exchanged zeolite X.

5. Conclusion

Zeolite X as well as ammonium-zeolite X was successfully synthesized and the soil-amendment capacity was effectively investigated with respect to plant growth at the vegetative stages. The investigation of the effect of ammonium-zeolite X (NH_4-LTX) on maize and okro showed significant increase in growth when NH_4-LTX was added to the soil. The most important factor was probably that the NH_4-LTX increased the supply of nutrients to the plants. Growth increased with the application of 5 % w/w LTX to soil with low nutrients. Ammonium-zeolite X has the attractive features for use as a potential soil amendment additive to improve plant growth. Therefore, it will be a better soil amendment additive compared to the conventional fertilizers which have to be applied periodically.

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