

**Synthesis Of Linde-Type X Zeolite And Its Application To  
Improve Soil Nutrients**

by

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## DECLARATION

I hereby declare that this submission is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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To  
Philemon Kwame Darkey,  
for all.

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## ABSTRACT

In this exploratory project, Linde-type X zeolite was synthesized and loaded with ammonium ions by ion exchange method. The ammonium exchange Linde-type X zeolite ( $\text{NH}_4\text{-LTX}$ ) was characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and Fourier transformed infrared (FTIR) spectroscopy. Surface morphological studies obtained from SEM photomicrographs showed the powdered synthetic zeolite X have a lamellar structure with cubical edge. SEM analysis also showed that the morphology of the zeolite particles was closely related before and after ion exchanged or before and after substitution of ammonium ions. XRD result showed that the phase of zeolite synthesized was similar to FAU. Also XRD analysis showed little or no changes in the phase purity of the Zeolite before and after ion exchange. Meanwhile, FTIR spectra exhibited the presence of internal Si-O-(Si) and Si-O-(Al) vibrations in the tetrahedral or alumino- and silico-oxygen bridge in the range of  $1200 - 400 \text{ cm}^{-1}$ . EDX and XRF results showed the concentration of  $\text{NH}_4$  loaded into the zeolite X framework. The effect of  $\text{NH}_4\text{-LTX}$  on maize and okro plants was evaluated with soil of low nutrients and a mixture of 5 % w/w and 95 % w/w soil of low nutrients was analyzed. The results showed significant difference ( $P = 2$ ) between plants in which  $\text{NH}_4\text{LTX}$  was added to the soil and plants with no  $\text{NH}_4\text{-LTX}$  when tested at 95 % confidence interval.

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## LIST OF ABBREVIATIONS



KNUST	Kwame Nkrumah University of Science and Technology
IZA	International Zeolite Association
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
EPA	Environmental Protection Agency
ppm	part per million
FAU	Faujasite
CBUs	Composite Building Units
EDX	Energy Dispersive X-ray
EDS	Energy Dispersed Spectrum
D6R	Double six rings
FTIR	Fourier Transformed Infrared Spectroscopy
ICDD	International Centre for Diffraction Data
TEM	Transmission Electron Microscopy
CEC	Cation Exchange Capacity
CSIR	Council for Scientific and Industrial Research
SRI	Soil Research Institute
E.C.E.C	Effective Cation Exchange Capacity
XRF	X-Ray Fluorescence
TGA	Thermo Gravimetric Analysis
T.E.B	Total Exchangeable Base

## **CHAPTER ONE**

### **INTRODUCTION**

#### **1.1 Introduction**

As agriculturalists all over the world increase their effort to expand production, more and more attention is being paid to various mineral materials as soil amendments (Mumpton, 1985). Crop production depends on the existence and maintenance of fertile soil. One group of minerals has emerged as having considerable potential in a wide variety of agricultural processes. This group of minerals is the zeolite group. The unique ion exchange, reversible dehydration, and adsorption properties of zeolite materials has shown great promise to contributing significantly for many years of agricultural technology (Mumpton, 1977).

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 (Polat et al., 2004). In this exploratory project, fertilizing capacity of laboratory-synthesized zeolite X was explored.

#### **1.2 Objectives of research**

The aim of this project is to investigate the fertilizing capacity of laboratory-synthesized zeolite X as a potential soil amendment. Specific objectives of this study include:

- (a) To synthesis zeolite X

- (c) To characterize the thermal, vibrational, morphological elemental composition of the synthesized zeolite X
- (d) To investigate the ability of zeolite X as potential soil amendment for maize (*Zea mays*) and okro (*Hibiscus esculentus*).

### **1.3 Justification of objectives**

Based on their high ion-exchange capacity and water retention, zeolites have been used extensively in Japan and Taiwan as amendments for soils (Hsu, 1967). The pronounced selectivity of zeolite X for cations such as ammonium and potassium has also been exploited in the preparation of chemical fertilizers that improve the nutrient-retention ability of the soils by promoting a slower release of these elements for uptake by plants (Fansuri et al., 2008).

### **1.4 Methodology**

The project was undertaken in two major stages, the first stage focused on the synthesis and the loading of the synthesized zeolite X with ammonium ions while the second stage was centered on the application of the synthesized ion exchange zeolite X to a soil of low nutrients to investigate its amendment effects on the soil. However the major activities undertaken during the project is detailed below:

#### **(a) Literature review**

Literature on zeolite and its application was gathered from various sources including the internet, the library and from Dr. B Kwakye-Awuah of the department of Physics, KNUST.



### **(b) Zeolite Synthesis (zeolite X)**

Zeolite X for the purpose of this project was crystallized hydrothermally at the Laboratory of the Water Research Group, based in the Department of Material Engineering, KNUST. The synthesis was based on the International Zeolite Association (IZA) standard method with some modifications.

### **(c) Characterization of the zeolites**

Characterization of the zeolites is detailed below:

X-Ray Diffraction (XRD) was used to identify the characteristics of the diffraction spectra and identify the zeolite type.

Energy Dispersive X-ray analysis was used to identify the elemental composition of the zeolite type.

Scanning Electron Microscope (SEM) was used to determine the morphology and size of the zeolite particles. It was also used to show the phase purity.

Thermo Gravimetric Analysis was used to determine the thermal stability of the zeolite.

Fourier Transform Infra Red was used to determine the vibrational properties of the zeolite.

### **(d) Ion exchange**

Ammonium ion was loaded into the zeolite X via ion exchange. The ammonium-exchanged zeolite X was again characterized as in (c).

**(e) Investigation of the fertilizing capacity of zeolite X**

Zeolite X was added to soils and tested on maize and okro. Both plants were harvested at weekly intervals from the date of germination to maintain constant growth cycle for comparing effects of zeolite X on plant growth. Harvesting comprised complete destruction of plant material from the point of stem emergence from soil, followed by measurement of plant height, number of leaves, leaf fresh weight, thickness of stem, leaf area and shoot dry weight.





## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Introduction

Superfund sites, large and small mining sites, landfills, and industrial sites such as refineries, smelters, foundries, milling and plating facilities, and other sites with contaminated or disturbed soils exhibit a variety of problems that often can be addressed effectively and directly through the use of soil amendments. These problems include (EPA, 2007):

- The toxicity of various soil contaminants, principally metals, can be harmful to plants, soil animals, and soil microbial populations.
- A higher or lower-than-normal soil pH range can cause soil infertility and cause soil metals (low pH) and oxyanions (e.g., arsenate at high pH) to go into solution.
- Excess sodium (Na) can cause toxicity to plants, a breakdown of soil physical structure, and dispersion, which limits root growth, aeration, and water infiltration through the soil.
- Excess salts (e.g., sulfates and chlorides) limit plant rooting and water and nutrient uptake.
- Changes in soil physical properties, such as density, aggregation, and texture, can reduce water infiltration and the moisture-holding capacity of the soil and stifle efforts to revegetate a site.
- Deficiencies in essential micronutrients like Zn and Mn can lower soil fertility; however, the same elements can be toxic at higher concentrations. In some cases, soil treatments to reduce phytotoxicity of one contaminant may reduce the phytoavailability of another essential element.

As soil amendment, zeolites consist of cage-like polyhedral units with a high cation-exchange capacity and internal pores in crystal lattices that result in high water adsorption and nutrient retention (Zelazny et al., 1977). Zeolite does not break down over time, but remains in the soil to improve nutrient retention. Therefore, its addition to the soil may significantly reduce water and fertilizer costs by retaining beneficial nutrients in the root zone. The porous structure of zeolite helps keep the soil aerated and moist as well as active for a long time (Ramesh et al., 2010). 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 (Wallace, 1998)

The most suitable soil for most plants is one with a good effective depth, favourable morphological properties, good internal drainage and an optimal moisture regime, sufficient and balanced quantities of plant nutrients and chemical properties that are favourable specifically for optimum production (du Plessis, 2003).

## **2.2. Soil**

Soils physically support plants, and act as reservoirs for the water and nutrients needed by plants. Soil is a natural body covering the earth's surface with biological, chemical and physical properties that gives the ability to support plant growth (Şen, 2003). Soils are complex mixtures of mineral particles of various shapes and sizes; living and dead organic materials including microorganisms, roots, and plant and animal residues; air; and water. In the soil, physical chemical and biological reactions occur constantly and are closely interre-

lated. The physical form of the soil plays a large role in influencing the nature of biological and chemical reactions. Optimum plant growth depends as much on a favorable physical environment as it does on soil fertility (Pansini, 1996).

Each soil type, in its complex structure, has a profile, which consists of some layers in the regolith part, extending down to the bedrock as shown in Figure 2.1.

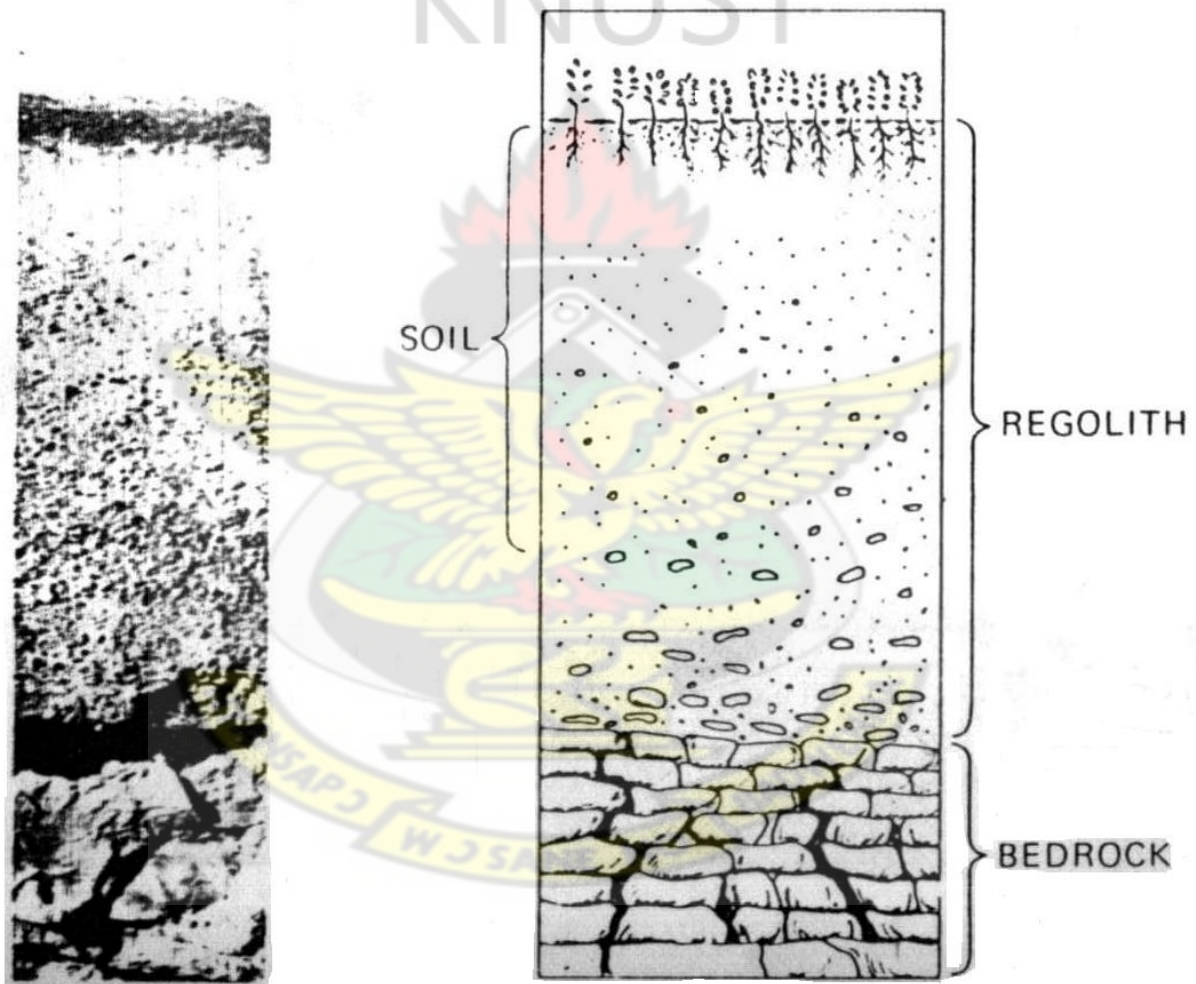


Figure 2.1: The portions of regolith, soil and bedrock (Buckmann et al, 1969)

Bedrock is the underlying rock on which the regolith portion is deposited. Regolith is all the loose material, formed by weathering of bedrock or by transportation action of wind, water or ice and thus displays great variations in composition from place to place. The upper part of the regolith is distinguished from the lower layers by the presence of roots of plants, soil organisms, high organic matter content, and minerals and by the presence of characteristic horizontal layers, which promote the growth of higher plants (Buckmann et al., 1969).

### **2.2.1 . Soil composition**

The solid portion of soil contains the mineral matter and organic matter. The mineral matter is formed from the parent rock, in other words the C-horizon. In addition, the organic matter is formed from the living organisms in soil. Besides the solid portion, water and air make up the pore space (Şen, 2003).

### **2.2.2 Soil profile**

Soil profile is the vertical section of soil exposing the layers as shown in Figure 2.2. The upper layer is called the A-horizon or topsoil, which is higher in organic matter content and darker in color than the layers below. B-horizon or subsoil is the middle part having relatively a brighter color and containing more clay. The A and B horizons together, are referred to as the true soil. The C-horizon, in other words parent material, can be thick, thin or even absent (Troeh et al., 1993).

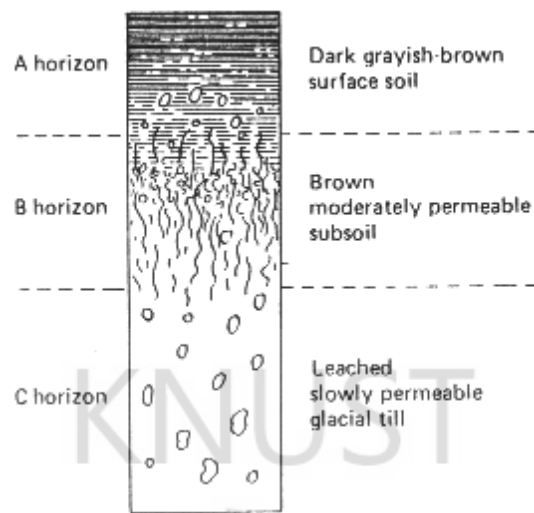


Figure 2.2 : Soil profile (Troeh et al., 1993)

### 2.2.3 Types of soil

Soil, according to its composition, is divided into two categories: mineral soils, and organic soils. Soils, formed in bogs and such wet areas, and containing more than 12-18% organic carbon (approximately 20 to 30 % organic matter) are called as organic soil (Şen, 2003). They consist of living microbes such as bacteria, fungi and living macro organisms such as plant roots, earthworms, insects and remains of dead macro organisms as well as the finally divided non-living organic materials. Organic soils are useful for high value crop production like fresh market vegetables when drained and cleared. They can also be prepared as organic supplements for home gardens and potted plants. Therefore, these soils submit an economical significance in localized regions.

Mineral soils occupy the highest portion of total land area and hence are considered as more important soils than organic soils. They are formed from rocks and sediments, in



other words they are the upper and biologically weathered portion of the regolith. A typical mineral soil contains approximately 45% mineral matter, 5% organic matter and 25% soil air and 25% soil water (Şen, 2003).

#### **2.2.4 Soil solution**

The soil solution is the interface between soil and the other three environmental active compartments (atmosphere, biosphere and hydrosphere). The soil solution is the source of mineral nutrients for all terrestrial organisms. As the soil solution percolates below the root zone, it becomes groundwater or drains to streams, lakes and other water bodies, this strongly affects their chemistry (Brady et al., 2002). The amounts of matter transferred are much greater and the rates of these reactions are much faster in the soil than in other environmental compartments. The soil solution is the most important transfer medium for the chemical elements that are essential to life.

The negative charge of soil particles in most soils extends electrically out into the soil solution. The soil solution differs from other aqueous solutions in that it is not electrically neutral and usually contains more cations than anions. These cations belong to the solid but are present in the solution. Soils in old and heavily weathered soils, as in parts of Australia, Africa and South America, or in soils of volcanic origin, as in Japan and New Zealand, may have a positive charge. There the soil solution has an excess of anions. Most soil reactions occur at the soil solution/soil interface (Bohn et al., 2001).

### 2.3 Plant nutrients

Plants contain more than 90 elements, but only 16 elements are recognized as essential. These elements are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, manganese, zinc, copper, molybdenum, boron and chlorine. Besides these, another four elements namely silicon, sodium, cobalt and vanadium might be beneficial to some groups of plants. Except carbon, hydrogen and oxygen, all the 13 essential elements are taken up by plants from soils and they are called mineral nutrients (Miah et al., 2005). Plants obtain carbon, hydrogen and oxygen from air and water.

The nutrients can be divided into two groups on the basis of the quantity required by the plants: macronutrients and micronutrients. Macronutrients are required relatively in larger quantities (usually above 0.1 % on dry weight basis) while micronutrients are required in smaller quantities (usually below 100 ppm). Carbon, Hydrogen and Oxygen constitute 90-95 % of plant dry matter weight. Nitrogen, Phosphorus and Potassium are called primary nutrients because of their large requirement and Calcium, Magnesium and Sulphur are called secondary nutrients (Miah et al., 2005).

Table 2.1 Plant nutrients and their sources (Buckmann et al., 1969)

Macronutrients		Micronutrients
Mostly from air and water	From soil	From soil
Carbon (C) Hydrogen (H) Oxygen (O)	Nitrogen (N) Sulphur (S) Phosphorus (P) Calcium (Ca) Potassium (K) Magnesium (Mg)	Iron (Fe) Manganese (Mn) Copper (Cu) Zinc (Zn) Boron (B) Molybdenum (Mo) Chlorine (Cl)

### **2.3.1 Nature and supply of plant nutrients**

Plants build up their biomass using water from soil, carbon dioxide from air, energy from sunlight and nutrients from soil (Miah et al., 2005). For optimum plant growth, nutrients must be available:

- as solutes in the soil water,
- in adequate and balanced amounts, corresponding to the instant demand of the crop, and
- in a form which is accessible to the root system (except when provided through foliage).

Plants obtain nutrients mainly from:

- Soil reserves,
- Mineral fertilizers,
- Organic sources,
- Atmospheric nitrogen through biological fixation,
- Atmospheric deposition, and
- Irrigation, flood and sedimentation

### **2.3.2 Functions of nutrients in plant**

Plants, like animals, require food for their growth and development. This food is composed of certain elements referred to as plant nutrients. The major functions of plant nutrients are given in Table 2.2



Table 2.2 Major functions of different nutrients in plants: (Miah et al., 2005)

Nutrient	Functions
Nitrogen (N)	Constituent of proteins, nucleic acids and chlorophyll
Phosphorus (P)	Constituent of nucleic acids and phospholipids; involvement in energy transfer
Potassium (K)	Enzyme activation; osmotic and ionic regulation
Sulphur (S)	Constituent of amino acids, biotin, vitamin B, and coenzyme A
Calcium (Ca)	Constituent of cell wall; role in cell division and permeability of cell membrane
Magnesium (Mg)	Constituent of chlorophyll; cofactor for enzymatic reactions
Iron (Fe)	Component of cytochromes, ferredoxins and leghaemoglobin
Manganese (Mn)	Involvement in oxidation-reduction reactions; formation of oxygen in photosynthesis
Copper (Cu)	Acts as an electron carrier; constituent of some enzymes e.g. cytochrome oxidase
Zinc (Zn)	Auxin formation; activation of dehydrogenase enzymes; stabilization of ribosomal fractions
Boron (B)	Regulates carbohydrate metabolism; involved in protein synthesis; role in seed formation
Molybdenum (Mo)	Constituent of nitrate reductase and nitrogenase enzymes
Chlorine (Cl)	Formation of oxygen in photosynthesis; role in osmoregulation

### 2.3.3 Nutrient deficiencies

Striking the appropriate balance in nutrients concentrations is essential, since many of these nutrients are also toxic in high concentrations. Deficiencies in phosphorus (P) and nitrogen (N) limit growth. Deficiencies in zinc (Zn), copper (Cu), manganese (Mn), and other nutrients that are necessary micronutrients also can lower soil fertility. In addition, proper ratios of calcium (Ca) to magnesium (Mg) and carbon (C) to nitrogen (N) are necessary for plant growth. As a rule-of-thumb, the C : N ratio is 15-40:1; the ideal Ca : Mg ratio

is no greater than 20 : 1. Higher C : N ratios will lead to immobilization of N. Soil microbes will scavenge for nitrogen and limit its availability for plants. In the case of lower C : N ratios, N will be in excess. This can lead to N leaching through the soil.

#### **2.3.4 Deficiency symptoms of nutrients in plants**

When a plant is deficient of a particular element, some characteristic symptoms appear. For example, when nitrogen is deficient, chlorophyll production is reduced and thus, the yellow pigments carotene and xanthophyll appear. Deficiency symptoms may vary from plant to plant species. Generally, deficiency symptoms are similar within a plant family since they have similar nutrient requirement.

Nutrient deficiencies are relative and a deficiency of one element implies adequate or excessive quantities of another. Thus, plants exhibit external symptoms of starvation as a result of nutrient deficiency or imbalance. For example, Manganese deficiency may be induced for adding large quantities of Iron. Hence, the same supply of Phosphorus may become sufficient or deficient depending on the level of Nitrogen supply.

It is often difficult to distinguish among the deficiency symptoms. The yellowing of leaves may appear due to a number of nutrient deficiencies. However, variation is noticed in leaf pattern or location on the plant. Further, disease or insect damage may resemble certain minor element deficiencies.

Table 2.3. Deficiency symptoms of various nutrients in plants (Miah et al., 2005).

Nutrient	Deficiency symptoms
Nitrogen (N)	Yellowing of older leaves; yellowing of whole leaves in case of severe deficiency, reduced tillering, stunted crop growth
Phosphorus (P)	Purple orange colour of older leaves while dark green of new leaves; reduced tillering
Potassium (K)	Older leaves may show spots or marginal burn starting from tips; increased susceptibility to diseases, drought, and cold injury
Sulphur (S)	Chlorosis of younger leaves; chlorosis of whole plant in severe cases
Calcium (Ca)	New leaves become white; growing points die and curl
Magnesium (Mg)	Marginal or interveinal chlorosis with pinkish colour of older leaves; sometimes leaf-rolling like drought effect; plants susceptible to winter injury
Iron (Fe)	Interveinal chlorosis of younger leaves; whole leaf may become first yellow and finally white in case of severity
Manganese (Mn)	Similar to iron deficiency; necrosis develops at advanced stage instead of white colour
Copper (Cu)	Chlorosis of young leaves, rolling and dieback
Zinc (Zn)	Rusting of leaves in rice, uneven crop growth, delay in maturity
Boron (B)	Pale green tips of blades, bronze tint; death of growing points, unfilling of grains
Molybdenum (Mo)	Mottled pale appearance in young leaves; bleaching and withering of leaves
Chlorine (Cl)	Wilting of leaflet tips; chlorosis of leaves leading to bronzing and dying

### 2.3.5 Availability of nutrients in soils to plants

Soil consists of mineral particles, organic matter, and pore spaces filled with air or water. The mixture of particle sizes (texture) and their arrangement in aggregates (structure) determine how well plant roots may grow in the soil and obtain from it the necessary water, air, and mineral nutrients. Soil color does not directly affect plant growth but sometimes

indicates conditions that affect plant growth. The layering of soil affects water penetration, aeration, and rooting depth. Soils deep and uniform in texture and structure are usually more productive and easier to manage than soils with barriers or abrupt changes in texture or structure within the normal plant root zone.

Nutrients can exist in the soil in various forms; dissolved in the soil solution, adsorbed on the soil particle surface or as constituents of the solid phase (sparingly soluble minerals, organic matter, and occluded material). These sources are not independent; inter-conversions between them are possible. The availability of a nutrient refers to that fraction of the nutrient which is accessible to plant roots. It is often observed that the total status of a particular nutrient in soil is high but the plants grown on this soil suffers from deficiency of that element (Miah et al., 2005). This indicates, the extent of availability is a big concern in question of plant uptake and consequent growth. Thus, a portion of the total content becomes available for plant uptake depending on some soil conditions, namely soil pH, soil texture, organic matter content, flooding, nutrient interaction, and temperature.

Table 2.4 Soil conditions inducing nutrient deficiency of crops (Miah et al., 2005):

Nutrient	Major conditions inducing deficiency
Nitrogen (N)	Low organic matter, submerged soils, burning of crop residues
Phosphorus (P)	Acidic, organic, leached and calcareous soils
Potassium (K)	Sandy, organic, leached and eroded soils
Sulphur (S)	Low organic matter, submerged soils, burning of crop residues
Calcium (Ca)	Acidic, alkali and sodic soils
Magnesium (Mg)	Acidic, alkali and sodic soils
Iron (Fe)	Calcareous soils, high soil P, Mn, Cu or Zn, high $\text{HCO}_3$
Manganese (Mn)	Sandy soils, calcareous soils, high organic matter, high soil Fe, Cu or Zn
Copper (Cu)	High soil N, P, or Zn
Zinc (Zn)	Calcareous soils, saline soils, submerged soils, low organic matter, high soil P, Ca, Mg, or Cu
Boron (B)	Sandy soils, high pH soils, dry soils
Molybdenum (Mo)	Calcareous soils, acid soils with high free Fe content

## 2.4. Soil amendments

Many soils, particularly those found in urban, industrial, mining, and other disturbed areas suffer from a range of physical, chemical, and biological limitations. These include soil toxicity, too high or too low pH, lack of sufficient organic matter, reduced water-holding capacity, reduced microbial communities, and compaction (EPA, 2007). Appropriate soil amendments may be inorganic (e.g., liming materials), organic (e.g., composts) or mixtures (e.g., lime-stabilized biosolids). When specified and applied properly, these beneficial soil amendments limit many of the exposure pathways and reduce soil phytotoxicity (Gruener et al., 2003).



Soil amendments can also restore appropriate soil conditions for plant growth by balancing pH, adding organic matter, restoring soil microbial activity, increasing moisture retention, and reducing compaction (Xiubin and Zhanbin, 2001). However, the appropriate use of soil amendments is completely dependent upon appropriate characterization of both the site and the residual materials to be employed.

Soil amendments can reduce the bioavailability of a wide range of contaminants while simultaneously enhancing revegetation success and, thereby, protecting against offsite movement of contaminants by wind and water. As such, they can be used in situations ranging from time critical contaminant removal actions to long-term ecological revitalization projects (Ming and Allen, 2001).

The high ion-exchange and retention ability of zeolites as well as their large adsorptive affinity for water has contributed to their successful applications in soil amendment (Polat, 2004). 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 (Beiersdorfer et al., 2003). Consequently this leads to more effective use of fertilizers by reducing their rates for the same yields, by prolonging their activity or finally by producing higher yields. This has been exploited in the preparation of slow-release chemical fertilizers (Mumpton, 1985).

Another beneficial property of zeolites in plant growth is its ability to trap heavy metals in the soil by ion-exchange and thereby preventing their uptake into the food chain. The origin of the heavy metals is often municipal and industrial sewage sludge used as a nutrient source.

## 2.5 Zeolites

Zeolites are crystalline aluminosilicates, compositionally similar to clay minerals, but differing in their well-defined three-dimensional nano- and micro-porous structure.

Aluminum, silicon, and oxygen are arranged in a regular structure of  $[\text{SiO}_4]^-$  and  $[\text{AlO}_4]^-$  tetrahedral units that form a framework with small pores (cavities) of about 0.1-2 nm diameter running through the material.

These units are assembled into secondary polyhedral building units such as cubes, hexagonal prisms, octahedra, and truncated octahedra. The silicon and aluminum atoms, located at the corners of the polyhedra, are joined by shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline framework. The tetrahedral can be arranged in numerous ways, resulting in the possibility of some 800 crystalline structures, less than 200 of which have been found in natural deposits or synthesized in laboratories around the world (Thompson, 1998).

Zeolites have a general formula



where

x and y are integers with y/x equal to or greater than 1,

n is the valence of cation M, and

z is the number of water molecules in each unit cell (Yang, 2003).

Identification of zeolites as a mineral goes back to 1756, when a Swedish mineralogist, Alex Fredrik Crönstedt, collected some crystals from a copper mine in Sweden. Zeolites mean ‘boiling stones’ in Greek, because of their ability to froth when heated to about 200°C. Thereafter, zeolites

were considered as a mineral found in volcanic rocks for a period of 200 years. Their commercial production and use started in the 1960s (Ramesh et al., 2010).

### 2.5.1 Zeolite structure

Although zeolites are crystalline, they have complex structures and large unit cells. Further, the diffraction techniques that are the workhorse of crystal structure analysis provide only an averaged view of the structure, in which local orderings or local deviations from the mean are represented merely as disorder. Our present understanding of zeolite structure thus derives from a combination of techniques (Newsam, 1986).

The crystal structure of a zeolite consists of windows, cages, and supercages. The windows are how the molecules reach the cages and supercages to be adsorbed or catalyzed. The cages are the smaller cells in the crystal structure. The supercages are cells in the crystal structure that are larger than cages and may even contain cages (EPA, 1998).

The zeolite structure is made up of  $\text{SiO}_4$  and  $\text{AlO}_4^-$  tetrahedra, linked together with adjacent tetrahedra sharing oxygen to form distinctive crystalline structures (framework structures). They contain large vacant spaces (cages) that can accommodate cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ), as well as large molecules and cation groups ( $\text{H}_2\text{O}$ ,  $\text{NH}_4^+$ ). The cations are mobile throughout the structure and play a charge balancing role with the  $\text{AlO}_4^-$  tetrahedra (Huang et al., 1994). The cage structures of zeolites are interconnected in three dimensions by channels of constant diameter. Only molecules with a small enough size to pass through channels can enter the internal structure of the zeolite (geometrical selectivity). These void spaces can be filled with water (or other molecules), which can be driven off and reabsorbed without changing the framework structure. The charge balancing cations



( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ) can be exchanged with other cations in aqueous solution, without affecting the aluminosilicate framework (Elliot et al., 2005).

Different zeolites have different selectivity for different cations, a strong selectivity for a particular ion will see that ion preferentially exchanged into the zeolite, and the non-selective species preferentially released into solution. These properties distinguish zeolites as a unique material and are important in its application. For many applications, like controlled release fertilisers, most zeolites will suffice (Elliot et al., 2005).

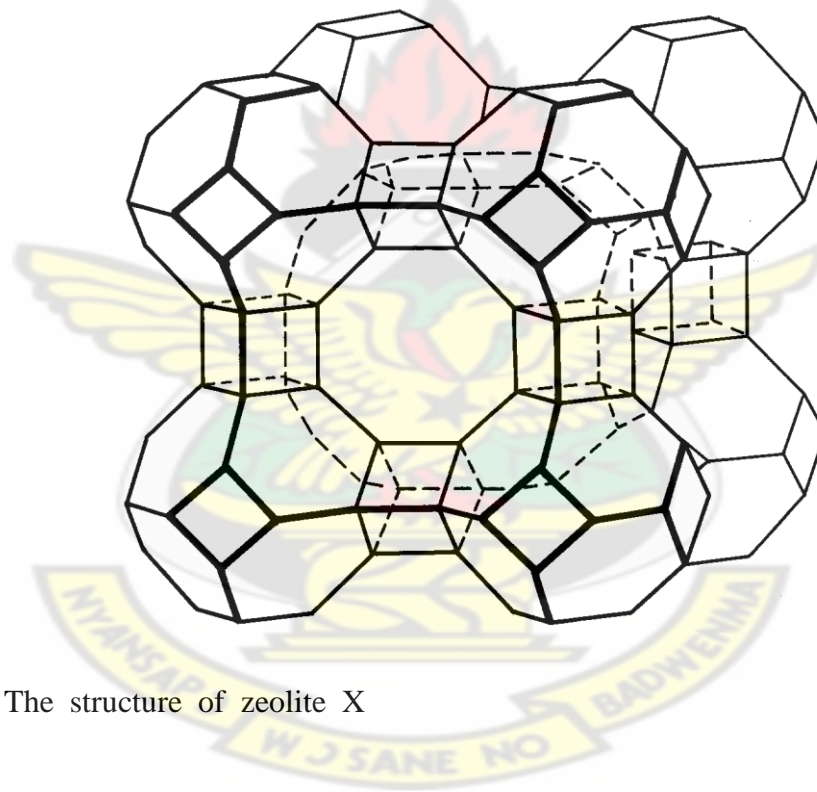


Figure 2.3: The structure of zeolite X

### 2.5.2 Linde-type X zeolite

Zeolite X is a large-pore zeolite with the same framework structural type as faujasite (FAU) but markedly different in framework composition and properties. Zeolite X has a Si/Al ratio of approximately 1.25 ( $[\text{AlSiO}_4]$ ). Zeolite X is an adsorbent and can be used in gas drying.

The composite building units (CBUs) of the FAU framework type are depicted in figure 2.4. The three CBUs are the double 6-ring, the sodalite cage, and a very large cavity with four 12-ring windows.

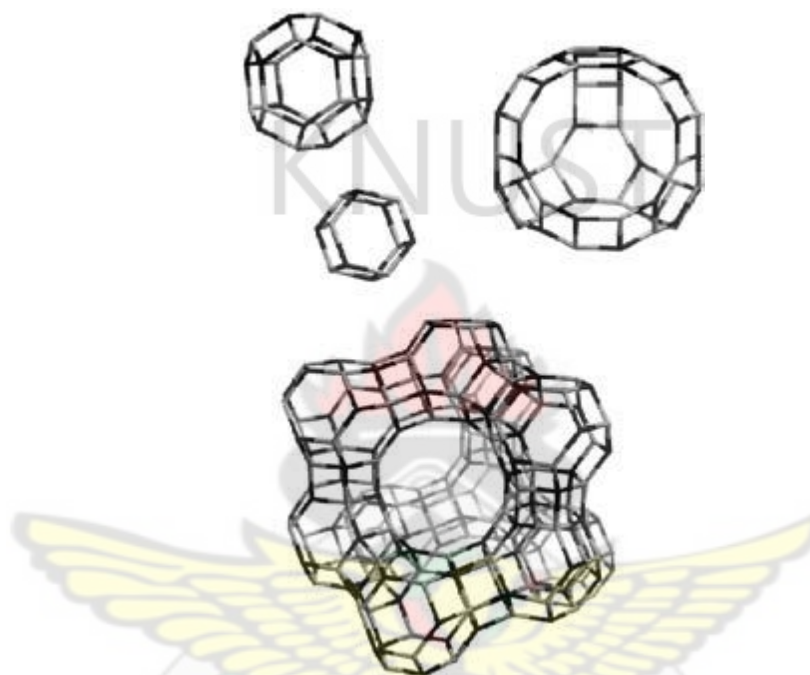


Figure 2.4: CBUs and framework structure of the zeolite X. (Handbook of Zeolite Science and Technology)

This cavity is of tetrahedral symmetry and it is known as the supercage. The connectivity of this cage allows molecules to diffuse in three dimensions in the crystal interior. This may not seem obvious by looking just at the cage, but a careful look at the periodic structure reveals that molecules can indeed travel in three directions. Zeolite X belongs to the  $Fd\bar{3}$  space group.

The lower symmetry of the zeolite X is the result of the ordering of the  $[\text{SiO}_4/2]$  and  $[\text{AlO}_4/2]$  tetrahedra. A unit cell contains eight large cavities (supercages), 8 sodalite cages, and 16 double 6-ring units. The 12-ring windows, with a free diameter of  $7.4 \text{ \AA}$ , are per-

pendicular to the [111] directions, but because of the tetrahedral symmetry of the cavity there are no straight channels along this direction. Channels can be thought to run along the [110] directions. Molecules larger than water or ammonia can access only the supercages and cannot pass into the empty space inside sodalite cages. Thus, all reactions and the adsorption of most adsorbates are confined to the supercages (Auerbac, 2003). Zeolite X has a wide range of industrial application primarily due to the excellent stability of the crystal structure and a large available pore volume and surface area (Kwakye-Awuah et al., 2008).

### **2.5.3 Cation exchange sites in zeolite X**

Zeolite X has a larger alpha cage than other similar zeolites like zeolite A and has similar size beta cages. Typical exchangeable ion sites are shown with Roman numeral in Figure 6. Typical exchangeable ion sites are site II which is the 6-ring between the alpha and beta cages, II' recessed into the beta cage, II\* recessed into the alpha cage, and I in the hexagonal prism connecting two beta cages (Auerbac, 2003).

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite cavities. The chemical composition can vary according to the silicon and aluminum content from a Si/Al ratio = 1.0-1.5 (Kwakye-Awuah et al., 2008).

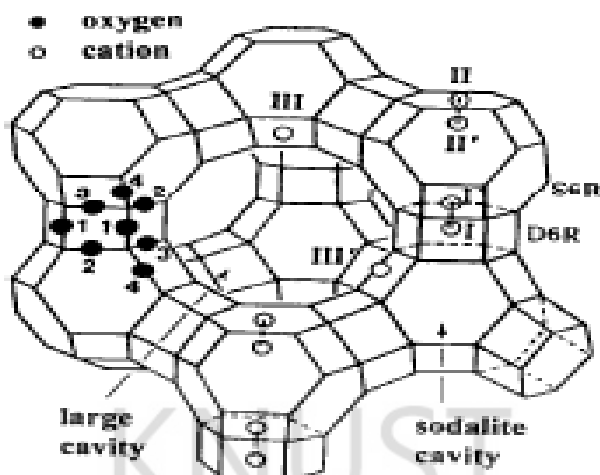


Figure 2.5 : Framework structure of zeolite X showing location of exchangeable sites

## 2.6 Characterization of zeolites

In general, the characterization of a zeolite has to provide information about structure and morphology, the chemical composition, the ability to adsorb and retain molecules and the ability to chemically convert these molecules. Information on the structural, chemical and catalytic characteristics of zeolites is essential for deriving relations between their chemical and physicochemical properties on the one side and the adsorptive and catalytic properties on the other. Such relations are of high importance, as they allow the rational development of adsorbents, catalyst and advanced structural materials (Malek, 2007).

The characterization techniques used in this study are X-ray Diffraction (XRD), Energy Dispersive X-ray analysis (EDX) and Fourier Transformed Infrared spectroscopy (FTIR). Microscopy method used was Scanning Electron microscopy (SEM). Each of the characterization techniques will be described below.

## 2.6.1 X-ray Diffraction (XRD)

### (a) Introduction

For zeolites produced in the laboratory, X-ray powder diffraction data is the most commonly used to validate the synthesized zeolite and to identify a newly synthesized material as well as to monitor the effects of a post-synthesis modification.

XRD provides the most comprehensive description of members of zeolite groups. The theory is based on the elastic scattering of X-rays from structures that have long range order. XRD is used to monitor the phase purity and crystallization and the purity of the zeolite particles. XRD also gives information of the particle strain and lattice size.

The X-ray diffraction technique is based on the Bragg's Law. The Bragg approach to diffraction is to regard crystals as built up of layers or planes such that each acts as a semi-transparent mirror. Some of the X-rays are reflected of a plane with the angle of reflection equal to the angle of incidence, but the rest are transmitted to be subsequently reflected by succeeding planes.

The general relationship between the wavelengths of incidence X-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg's law:

$$n\lambda = 2d \sin\theta$$

2

Where:

n (an integer) is the "order" of reflection

$\lambda$  is the wavelength of the incident X-rays

d is the inter-planar spacing of the crystal and

$\theta$  is the angle of incidence.

The primary use of Bragg's law is in the determination of the spacing between the layers in the lattice for, once the angle  $\theta$  corresponding to a reflection has been determined,  $d$  may readily be calculated from

$$d_{hkl} = \frac{n\lambda}{2 \sin \theta} \quad 3$$

#### (b) Principle of XRD

The mostly used XRD technique for zeolites is the powder diffraction technique because zeolite is mainly in the powder form. Powder diffraction techniques are used to identify a sample of a solid substance through the comparison of the positions of the diffraction lines and their intensities with a large data bank which can be acquired from the powder diffraction file, maintained by the International Centre for Diffraction Data (ICDD) and contains information of about 50 000 crystalline phases (Malek, 2007).

A monochromatic beam of X-rays strikes a finely powdered sample that, ideally, has crystals randomly arranged in every possible orientation. In such a powder sample, the various lattice planes are also present in every possible orientation. For each set of planes, therefore, at least some crystals must be oriented at the Bragg angle,  $\theta$ , to the incident beam and thus, diffraction occurs for these crystals and planes. The diffracted beams may be detected by surrounding the sample with a detector.

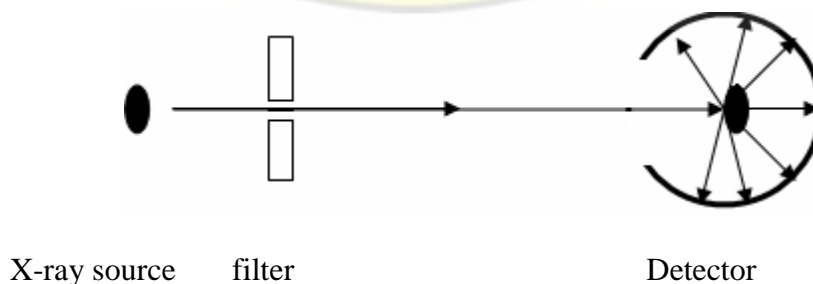


Figure 2.6 The illustration of the X-ray powder diffraction method



## **2.6.2 Energy Dispersive X-ray spectroscopy (EDX)**

### **(a) Introduction**

Energy Dispersive X-ray Analysis (EDX) is employed in Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for local elemental identification. The incident electron beam induces X-ray fluorescence in the sample which is energy-analyzed using a cooled semiconductor detector. The element-specific spectral lines are then identified to give the local elemental composition. EDX is used in many different application areas such as in the chemical, electronic and food industries as well as refineries. It can be used with solid, powder and frozen liquid samples.

### **(b) Principle of EDX**

Most EDX equipments are fitted in conjunction to a scanning electron microscope (SEM). The EDX measures the energy of X-rays that are generated by the atoms of the sample during interactions with the electron beam. The X-ray spectra formed are characteristic of the atoms that formed them, allowing the chemical composition of the sample to be determined.

## **2.6.3 Scanning Electron Microscopy**

### **(a) Introduction**

Scanning Electron Microscopy is a versatile and well-established complementary technique to light optical microscopy. By using a beam of electrons instead of photons, samples can be imaged at far higher magnifications.

#### (b) Principle of SEM

SEM can use different signals to generate contrast mechanisms. The back-scattered electron and secondary electron signals can be used to form images that can give information about the structure, topography and compositional features of a sample

### **2.6.4 Fourier transformed infrared spectroscopy (FTIR)**

#### (a) Introduction

FTIR spectroscopy is used to investigate the structural features of samples.

#### (b) Principle of FTIR

The principle of FTIR used in this study is based on the principle of diffuse reflectance. Incident light from a source radiation is scattered in all directions. These spectra can exhibit both absorbance and reflectance features due to contributions from transmission, internal and specular reflectance components, and the scattering phenomena in the collected radiation. A monochromator (usually a salt prism or a grating) separates a source radiation into different wavelengths that are collected by a slit system. A beam splitter separates the radiation into two: half goes through the sample and half to a reference.

A detector collects the radiation that passes through the sample, compares its energy to that going through the reference and sends it to a recorder (computer connected to the instrument). The recorder is calibrated in such a way that it converts the radiation into energy signals which is presented as a function of frequency.



## 2.7 Cation exchange capacity of zeolite

Because zeolites are composed of crystalline aluminosilicates with the structure based on tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  units, connected by shared oxygen atoms, they are one of the synthetics inorganic cation-exchangers. This kind of three dimensional structure has small pores where the exchangeable ions are located and where the ion exchange reactions take place. Silicon is tetravalent and aluminium is trivalent, which result in negatively charged framework structures. Thus each mole of aluminium produces one equivalent of cation exchange capacity for the zeolite framework. Ion exchange is a chemical reaction in which free mobile ions of a solid, the ion exchanger, are exchanged for different ions of similar charge in solution.

The exchange reactions in typical zeolite can be written as follows:



Where:

$\text{M}^+ \text{X}^-$  = Zeolite with  $\text{M}^+$  is framework and  $\text{X}^-$  is counter ion.

$\text{N}^+$  = Cation in the solution

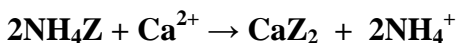
The cation exchange behavior depends on the nature of the cation, its size and charge, the temperature, the concentration of cations in solution, the anions and the solvent, and the structure of the zeolite. As a general rule, the equilibrium selectivity favors cations of a higher valence. The selectivity favors cations with a higher atomic weight for those with the same valence. The selectivity follows the relative order of free energies of reaction for different cations, favoring the reaction with the most negative free energy of reaction (Yang, 2003). Cation exchange capacity (CEC) is commonly measured in terms of moles of exchangeable cation per gram (or 100 grams) of zeolites, moles/g or in terms of equi-

valents of exchangeable cation per gram (or 100 grams) of zeolites, meq/g. Using CEC expressed in terms of miliequivalents per gram (meq/g) makes it easy to compare how much of any cation can be exchanged by a particular zeolite, without having to worry about the charge on the cation involved (Malek, 2007).

## 2.8 Using ammonium exchanged zeolite X to improve soil nutrients

Cation exchange is a reversible chemical reaction between cations (eg plant nutrients  $K^+$ ,  $NH_4^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) in the solid phase (eg zeolite) and in solution (eg water in soil). The behaviour of this exchange will depend upon the selectivity of the zeolite. For a non-selective zeolite, all nutrients are exchanged into the lattice and are released to maintain the same cation ratios in solution as in the zeolite. A dynamic equilibrium occurs where the zeolite behaves as a general ion buffer. However by the nature of ion exchange reactions, ion exchangers always exhibit a greater selectivity or affinity for particular ions over others, and have an ordered selectivity sequence for cations. Due to differences in pore size and framework charge, different zeolites have different selectivity for different elements (Elliot et al., 2005).

Zeolite X loaded with  $NH_4^+$ , and applied as a fertiliser onto the soil, will result in the exchange  $NH_4^+$  ions from the zeolite to water in the soil to maintain an equilibrium concentration in the soil. As  $NH_4^+$  are stripped from the soil by plants, more is released by the zeolite X to maintain a dynamic equilibrium between the soil and the zeolite X. In conjunction with the release of  $NH_4^+$  ions, other ions in the soil, such as  $Ca^{2+}$  will be exchanged into the zeolite lattice to maintain charge neutrality.



## CHAPTER THREE

### METHODOLOGY AND EXPERIMENTAL DESIGN

#### 3.1 Synthesis of zeolite X

Zeolite X (crystal composition:  $\text{Na}_{80}[\text{Si}_{112}\text{Al}_{80}\text{O}_{384}]\cdot 260\text{H}_2\text{O}$ ) was synthesized based on the International Zeolite Association (IZA) standard method with some modifications. The batch composition for the synthesis is given by:

**5.5  $\text{Na}_2\text{O}$ : 1.65  $\text{K}_2\text{O}$ :  $\text{Al}_2\text{O}_3$ : 2.2  $\text{SiO}_2$ : 120  $\text{H}_2\text{O}$**

**6**

The source materials were distilled water sodium hydroxide (45.6 %  $\text{Al}_2\text{O}_3$ , 29.65 %  $\text{Na}_2\text{O}$ ), potassium hydroxide (reagent grade, 86 % KOH), sodium aluminate (reagent grade, 97 % NaOH) and sodium silicate solution (28.7 %  $\text{SiO}_2$ , 8.9 %  $\text{Na}_2\text{O}$ )

#### Batch preparation

22.37 g of sodium aluminate powder was dissolved in 30 ml of distilled water while stirring until a homogeneous solution was obtained. In a separate vessel, 31.09 g of sodium hydroxide and 21.53 g of potassium hydroxide were added to 70 g of distilled water while stirring until a homogeneous solution was obtained. The sodium aluminate suspension was added to the potassium hydroxide and 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

funnel and Whatman No 1 filter paper. The powder samples obtained were washed copiously with distilled water. Following overnight drying of the powdered zeolite at 80 °C in an electrical oven, the zeolite was crushed into uniform powder with pestle and mortar, sieved and stored in a cupboard.

### 3.2 Ammonium ion ( $\text{NH}_4^+$ ) exchange in zeolite X

The ammonium ion exchange process occurs when  $\text{NH}_4^+$  from solution replace counter ions within the crystal structure. In the cation exchange process,  $\text{NH}_4^+$  move from the bulk solution to a zeolite dependant stagnant water layer which surrounds the zeolite particle. After diffusion through this film, the cations ( $\text{NH}_4^+$ ) often have to dehydrate partly in order to enter the zeolite pores and channels. The exchange process is defined by;

$$Q = \frac{V(C_0 - C_e)}{M} \quad 7$$

Where

Q is the  $\text{NH}_4^+$  exchanged on zeolite X,

M is the mass of zeolite X,

$C_0$  and  $C_e$  are the initial and equilibrium concentrations of  $\text{NH}_4^+$  in solution respectively,

and V is the volume of the solution.

The removal efficiency E is given by the equation;

$$E = \frac{(C_0 - C_e)}{C_0} \quad 8$$

### Batch ammonium 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 °C in an electric oven and crushed. This process was repeated for three more times to obtain significant ion exchange.

### 3.3 Experimental method

Samples of zeolite X and ammonium exchanged zeolite X were parcelled and sent to Prof. William Craig of the University of Wolverhampton for characterization, via DHL.

### 3.4 Pot plant trials

To assess the effect of zeolite X application as soil amendments for plant, a pot experiment was carried out for a period of six weeks. Soil of low nutrients was obtained from Council for Scientific and Industrial Research (CSIR) Crop Research Division, Kwadaso, Kumasi. Two plant species were used; maize (*Zea mays*) and okro (*Hibiscus esculentus*). Plants of each species were planted in a soil-zeolite X mixture (95:5 weight/weight combination) with untreated soil (100% soil by weight) as control.

In total, 32 maize plants and 32 okro plants were used, which means four groups with 16 plants per group. The plants of the control group were planted in soil with no addition of zeolite X. The treatments were 5% zeolite with 95% low nutrient soil and 100 % low nutrient soil only. All soil samples were sieved through a 2mm sieve before application. Normal cultural practices for raising a successful crop were applied uniformly to all the

experimental units. The plots were hand weeded at different growth stages. Irrigation was applied at regular intervals. A set of basic plant measurements were recorded during the course of study to evaluate the growth rate of the plants. Basic plant measurements data were recorded on alternate week to evaluate the development phases of growth and development of the plants.

#### **3.4.1 Soil sample collection and preparation**

Soil sample obtained from CSIR Soil Research Institute, Analytical Services Division was air-dried, ground and sieved to pass through a 2-mm sieve. The following chemical analyses were done on the soil sample, using standard laboratory methods: soil pH (soil : water ratio of 1:1); organic carbon; total nitrogen, organic matter; exchangeable cations (Ca, Mg, K and Na); total exchangeable base; exchangeable acidity (Al + H); effective cation exchange capacity (E.C.E.C); base saturation; and available P and K (using Bray-1 method) were determined on the soil.

#### **3.4.2 Data collection**

Data collection started seven days after planting. Growth parameters recorded at different stages of crop growth and development were: plant height, number of leaves, stem girth, leaf area, wet weight and dry weight. These parameters were determined in the following ways;



### **Plant height**

This was taken from a sample of three randomly selected plants marked within each plot. A carpenter's tape was used for measuring the height from the ground level to the whorl of the plant. The mean from the three plants were then determined.

### **Number of leaves**

Visual counting of leaves on the three randomly selected plants was made and the number was recorded for each plant. The mean values were then calculated for each plot.

### **Stem girth**

The stem width of the tree selected plants was measured with a micro meter screw gauge at three different locations along the stem and the average value recorded.

### **Leaf area**

The outline of the biggest leaf on each of the three randomly selected plant from each plot was carefully trace out on a graph paper using a pencil. The area of the leaf was then determine by counting the small boxes within the traced outline of the leaf.

### **Fresh weight**

Three randomly selected plants from each plot were remove from soil and wash off any loose soil. Plants were blot gently with soft paper towel to remove any free surface moisture and weighed immediately (plants have a high composition of water, so waiting to weigh them may lead to some drying and therefore produce inaccurate data).

### **Dry weight**

Since plants have a high composition of water and the level of water in a plant will depend on the amount of water in its environment (which is very difficult to control),

using dry weight as a measure of plant growth tends to be more reliable. The three plants randomly picked from the soil were dried in an oven at 70 °C for 48 hours. The plants were allowed to cool in a dry environment (Ziploc bag) and the weight taken.

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## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Synthesis, ion exchange and characterization of zeolite X

The results based on the synthesis, ion exchange and the characterization of zeolites X together with ammonium loaded zeolite X before and after ion exchange are presented.

##### 4.1.1 Synthesis of zeolite X

As discussed in section 3.0 the batch composition for the synthesis is given by:

**5.5 Na<sub>2</sub>O: 1.65 K<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 2.2 SiO<sub>2</sub>: 120 H<sub>2</sub>O**

Two attempts using the above gel composition were made. With the first unsuccessful and the second successful.

##### 4.1.2 Ion exchange

Ion exchange was carried out on synthesized zeolite X as described in Section 3.2. The ammonium exchanged zeolite X was parcelled and mailed to Prof. W. Craig for characterization by SEM, XRD, EDX and FTIR. The value of the cation exchange capacity of zeolite X is 4.73 meq/g.

##### 4.1.3 Characterization

The SEM micrographs of zeolite X (figure 4.1 a) and ammonium exchanged zeolite (figure 4.1 b) confirming the phase purity of the crystal morphology is shown in figure 4.1

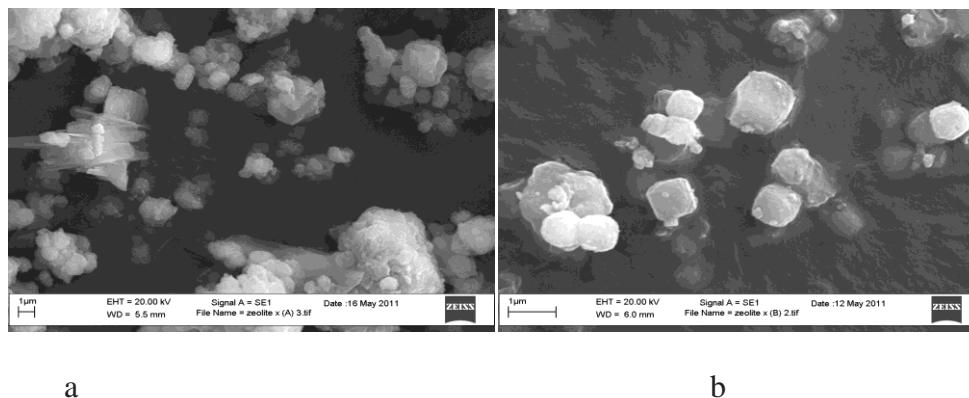


Figure 4.1: SEM micrographs of zeolite X (a) and ammonium exchanged zeolite X (b) showing varying sizes

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. EDX spectrum detected ammonium ions in the zeolite framework as peaks of nitrogen after loading

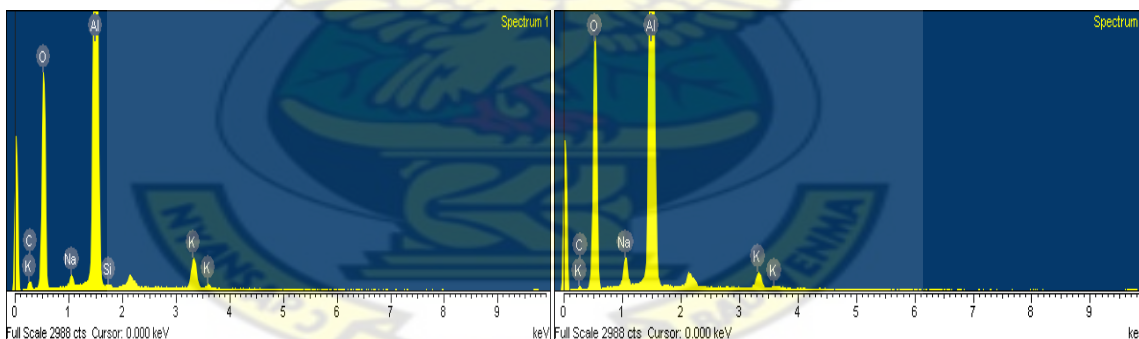


Figure 4.2: EDX spectra of zeolite X without (left) and with (right) ammonium loading

The structural features in the zeolite X and ammonium exchanged zeolite X frameworks were analyzed by FTIR which gives information on two classes of vibration:

- (1) vibrations caused by internal stretching of the framework tetrahedra
- (2) vibrations related to the external linkages between tetrahedral

Table 4.1: General infrared assignments in Zeolites (Flanigen et al., 1978; Kwakye-Awuah et al., 2008)

Internal vibrations		External T – O linkages	
Asymmetric stretch	1250 – 950	Double ring	650 – 500
Symmetric stretch	720 – 650	Pore opening	420 – 300
T – O bend	500 – 420	Symmetric stretch	750 – 820
		Asymmetric stretch	1150– 1050
Internal vibrations		External T – O linkages	
Asymmetric stretch	1250 – 950	Double ring	650 – 500
Symmetric stretch	720 – 650	Pore opening	420 – 300
T – O bend	500 – 420	Symmetric stretch	750 – 820
		Asymmetric stretch	1150 – 1050

Although each zeolite has a characteristic FTIR pattern some common features are observed for all zeolites (Kwakye-Awuah et al., 2008).

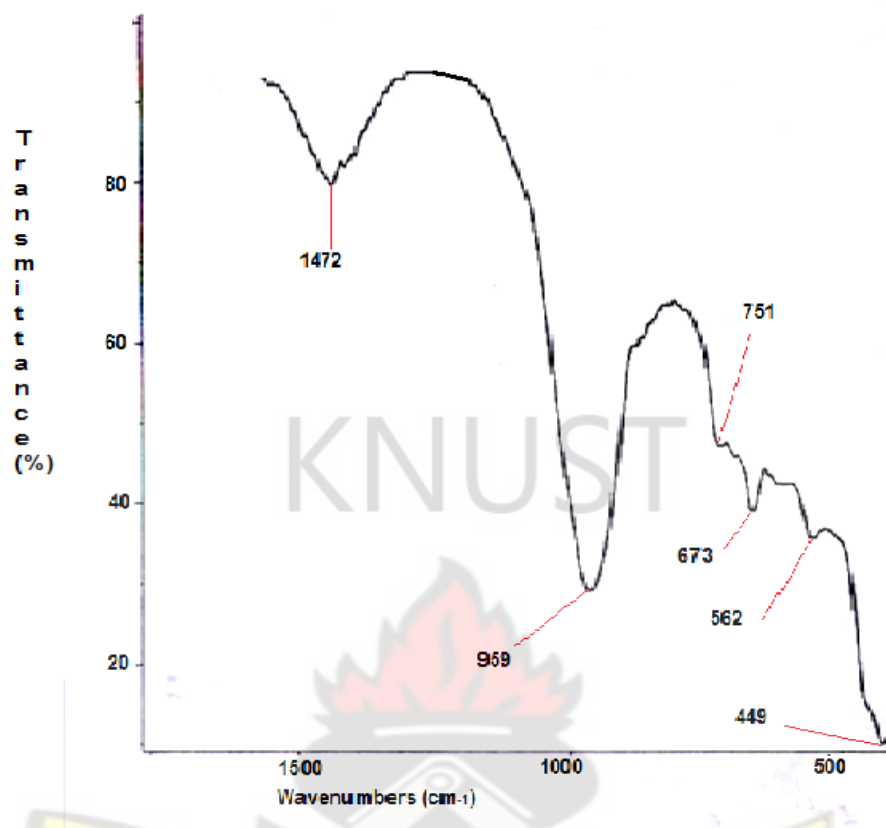


Figure 4.3: Results of the FTIR spectra of zeolite X.

The mid-FTIR spectrum of the as-synthesized zeolite X is given in Figure 4.3 in the region of lattice vibrations ( $1500 - 400 \text{ cm}^{-1}$ ). A large broad band was observed in the region  $950 - 960 \text{ cm}^{-1}$  in both samples. This band can be attributed to the overlap of the asymmetric vibrations of Si – O (bridging) and Si – O<sup>-</sup> (non-bridging) bonds. The band shifted towards a higher frequency of  $1374 \text{ cm}^{-1}$ . The symmetric stretching of the external T – O linkages occurred at  $751 \text{ cm}^{-1}$  whilst the symmetric stretching due to the internal vibrations of the zeolite X framework tetrahedra occurred at  $673 \text{ cm}^{-1}$ . Vibrations associated with the double six rings (D6R) that connect the sodalite cages occurred at  $562 \text{ cm}^{-1}$ . The band at  $449 \text{ cm}^{-1}$  is assigned to the internal vibrations due to the bending of the T – O tetrahedra.



The quantitative determination of major elements contained in the zeolite samples was physical analysis method using the wavelength dispersive X-ray fluorescence (XRF) technique. The percent amount of these elements from XRF technique before and after ammonium loading is given in Table 4.2. XRF results when compared before and after ion exchange showed a very clear trend of zeolite X, as a ammonium ion selective zeolite. XRF results in conjunction with TGA results determined the amount of ammonium ion exchanged into the zeolites shown in Figure 4.2

Table 4.2: Percentage amount of major elements contained in zeolite samples by XRF technique

Elements	LT X	Ammonim exchanged LTX
Na <sub>2</sub> O	17.09	13
Al <sub>2</sub> O <sub>3</sub>	29.65	29.65
SiO <sub>2</sub>	13.71	13.71
K <sub>2</sub> O	3.668	5.21
NH <sub>4</sub> OH		3.78

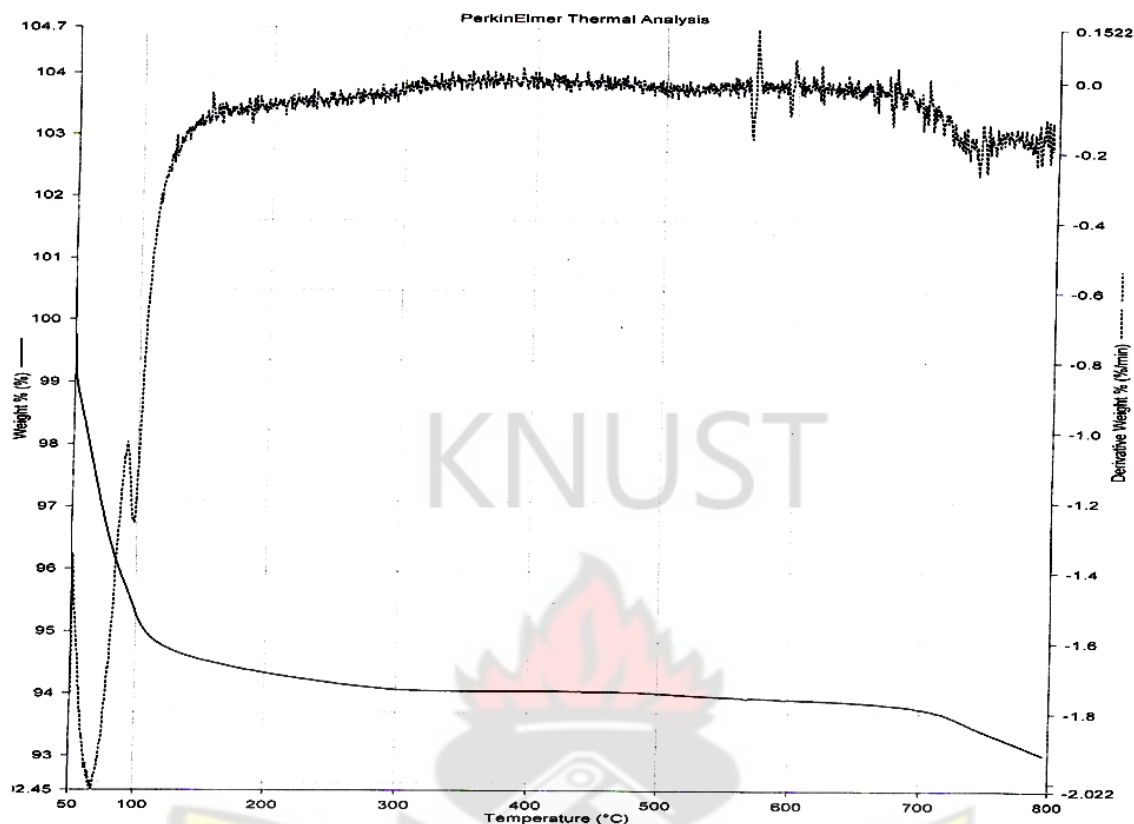


Figure 4.4: TGA spectrum of zeolite X

Very little water due to the absence of a major dip.

## 4.2 Soil analysis

The chemical properties of the soil prior to the addition of ammonium exchanged zeolite X and after the addition of ammonium exchanged zeolite X before planting is given in

Table 4.3: Chemical properties of soil.

Properties	values	
Soil properties	Before amendment	After amendment
pH 1:1 (H <sub>2</sub> O)	3.8	6.3
organic C (%)	0.45	0.45
total N (%)	0.04	0.33
organic M (%)	0.78	0.78
<b>Exchangeable cations (meq/100g)</b>		
Ca	0.80	0.8
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.(meq/100g)	2.87	4.95
Base salt (%)	40.77	91.90
<b>Available-Bray's</b>		
ppm P	<b>0.16</b>	14.54
ppm K	<b>26.78</b>	544.39

### Soil pH

Soil pH is a measure of soil acidity (Marx, 1999). Most crops grow best if the soil pH is between 5.5 and 7.5. On application of the ammonium exchanged zeolite X to the soil, the pH increased from 3.8 to 6.3

### **Organic carbon and organic matter**

Maintenance of soil organic matter is one of the most important goals of soil management. Most methods employed in the measurement of soil organic matter are indirect and this is because it is difficult to accurately measure soil organic matter. Soil carbon is usually measured and an assumption is made about the percent carbon content of organic matter. Ammonium exchanged zeolite X had no noticeable effect on organic matter and organic carbon as seen in table 4.3.

### **Nitrogen N**

Nitrogen is available to plant as nitrate ( $\text{NO}_3$ ) and ammonium ( $\text{NH}_4$ ). Soil concentration of nitrate and ammonium depends on biological activity and therefore fluctuate with changes in conditions such as temperature and moisture. The total nitrogen which is a measure of N in all organic and inorganic forms increased from 0.04 to 0.33 which can be attributed to the ammonium loaded into the zeolite X.

### **Exchangeable cations**

Of the exchangeable cations sodium (Na) is not a plant nutrient, but excessive amounts negatively affects plant growth. Potassium requires the most management. Calcium (Ca) is usually deficient in acid soil hence its low value of 0.8 meq/100g. Magnesium (Mg) also recorded a low value of 0.27 meq/100g which falls below the optimum plant requirement which lies in the range of 0.5 to 1.5 meq/100g. Available Ca and Mg in the soil was not affected by the addition of ammonium exchange zeolite X to the soil.

### **Total exchangeable base (T.E.B.) and exchangeable acid (Al + H)**

T.E.B. is the sum of the exchangeable cations in the soil and this is due to the base while exchangeable acid is the sum of cations obtained from the acids in the soil.

### **Effective cation exchange capacity (E.C.E.C.)**

E.C.E.C. is a measure of the capacity of the soil to retain and release cations. It is the sum of T.E.B. and exchangeable acid. For an acidic soil as in this case, the E.C.E.C. is low, hence the low value of 2.87 meq/100g. However, on the application of ammonium exchanged zeolite X the value rose to 4.94 meq/100g due to the basic nature of zeolite X.

### **Base saturation**

Base saturation is the percentage of E.C.E.C. that is occupied by cations other than hydrogen (H) and aluminium (Al). Soil with low base saturation generally are acidic. Base saturation increases with pH increases. At a pH of 3.8, base saturation was 40.77 however on the addition of the ammonium exchanged zeolite X, the pH of the soil increased to 6.3 with its corresponding increase in base saturation of 91.90.

### **Available-Bray's**

The values of phosphorus (P) and potassium increased from 0.16 and 26.78 respectively to 14.54 and 544.39 respectively.

### **4.3 Growth parameters**

The fresh weight, dry weight, number of leaves per plant, stem thickness, stem length and leaf area grown in two different growth substrates after 42 days of growing period are shown below

#### **4.3.1 Growth parameters of maize plants**

All data collected were subjected to one-way analysis of variance on a computer package SPSS, version 17, for windows. Data were tested for homogeneity of variance and were also analyzed for least significant differences (LSD) within treatments.

#### **Plant height**

Plant height is an important morphological character that acts as a potent indicator for availability of growth resources in its vicinity (Khan et al., 2009). The height of a plant depends on nutrients especially on nitrogen (Ferdous, 2001). Plant height increased progressively in all treatments over time, however, there was significant difference between samples of different treatment ( $P = 0.000$ ,  $N = 2$ ) and no significant difference between samples of the same treatment ( $P = 0.061$ ,  $N = 2$ ) as shown in Table 4.4. The effect of zeolite application on plant height of the two treatment is illustrated in Figure 4.5. Similar trends was reported by Naik, (1989) and Akhtaruzzaman, (1998)



Table 4.4: Analysis of variance (ANOVA) of maize plant height (cm)

		Sum of Squares	df	Mean Square	F	Sig
<b>Between treatment</b>		<b>744.143</b>	<b>17</b>	<b>43.773</b>		
<b>Within treatment</b>	<b>Between samples</b>	<b>141.214</b>	<b>1</b>	<b>141.214</b>	<b>403.373</b>	<b>0.000</b>
	<b>Nonadditivity</b>	<b>1.204</b>	<b>1</b>	<b>1.204</b>	<b>4.060</b>	<b>0.061</b>
	<b>Balance</b>	<b>4.747</b>	<b>16</b>	<b>0.297</b>		
	<b>Total</b>	<b>5.951</b>	<b>17</b>	<b>0.350</b>		
	<b>Total</b>	<b>147.165</b>	<b>18</b>	<b>8.176</b>		
<b>Total</b>		<b>891.308</b>	<b>35</b>	<b>25.466</b>		

### Number of leaves

The number of leaves were determine by counting. There was no significant difference within samples of the same treatment ( $P = 0.001$ ,  $N = 2$ ), however there was significant difference between samples of different samples ( $P = 0.000$ ,  $N = 2$ ) as shown in Table 4.5. Figure 4.6 shows that the LTX + Soil treatment develop faster during the whole trial. These results are similar to those obtained for growth parameters of sorghum in a study by Agbede et al., (2008) and of maize by Adelekan et al., (2010) using poultry manure.

Table 4.5: Analysis of variance (ANOVA) of the number of leaves of maize plant

		Sum of Squares	df	Mean Square	F	Sig
Between treatments		99.139	17	5.832		
Within treatments	Between samples	23.361	1	23.361	77.281	0.000
	Non additivity	2.467	1	2.467	14.773	0.001
	Balance	2.672	16	0.167		
	Total	5.139	17	0.302		
	Total	28.500	18	1.583		
Total		127.639	35	3.647		

### Fresh weight

The ANOVA of the fresh weight of the maize plants are presented in Table 4.6. The LTX + Soil treatment clearly have the highest fresh weight of approximately 6.4 g at 42 DAP as compared to approximately 3.8 g at 42 DAP for the Soil only treatment as illustrated in Figure 4.7. A significant difference ( $P = 0.000$ ,  $N = 2$ ) can be seen between treatments, however there was no significant difference within treatments ( $P = 0.329$ ,  $N = 2$ ).

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 (Singh and Rajodia, 1989). It was observed that there was a substantial improvement in the growth and development due to the application of  $\text{NH}_4\text{-LTX}$ .

Table 4.6: Analysis of variance (ANOVA) of the fresh weight of maize plant

		Sum of Squares	df	Mean Square	F	Sig
<b>Between treatments</b>		$1.941 \times 10^7$	17	1141625.819		
<b>Within treatments</b>	<b>Between samples</b>	1150054.986	1	1150054.986	1.009	0.329
	<b>Non additivity</b>	$1.938 \times 10^7$	1	1.938E7	4875098.187	0.000
	<b>Balance</b>	63.607	16	3.975		
	<b>Total</b>	$1.938 \times 10^7$	17	1140039.751		
	<b>Total</b>	$2.053 \times 10^7$	18	1140596.153		
<b>Total</b>		$3.994 \times 10^7$	35	1141096.277		

### Dry weight

The dry weight of the maize plants are presented in Figure 4.8. The 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, but however there was significant difference between and within treatments ( $P = 0.000$ ,  $N = 2$ ) throughout the investigative period as shown in Table 4.7.

Table 4.7: Analysis of variance (ANOVA) of the dry weight of maize plant

		Sum of Squares	df	Mean Square	F	Sig
<b>Between treatments</b>		<b>2.797</b>	<b>17</b>	<b>0.165</b>		
<b>Within treatments</b>	<b>Between samples</b>	<b>0.451</b>	<b>1</b>	<b>0.451</b>	<b>153.150</b>	<b>0.000</b>
	<b>Residual</b>	<b>Non additivity</b>	<b>0.037</b>	<b>1</b>	<b>0.037</b>	<b>44.049</b>
		<b>Balance</b>	<b>0.013</b>	<b>16</b>	<b>0.001</b>	
		<b>Total</b>	<b>0.050</b>	<b>17</b>	<b>0.003</b>	
	<b>Total</b>	<b>0.501</b>	<b>18</b>	<b>0.028</b>		
<b>Total</b>		<b>3.297</b>	<b>35</b>	<b>0.094</b>		

Table 4.7 shows very large increases in the dry weight of plants grown in the amended substrates. This is thought to be due to a greater degree of mineralization of the soil pore water which increases the availability of plant nutrients (Leggo et al., 2006). The dramatic growth behavior is thought to be due to the release of ammonium ions from the  $\text{NH}_4\text{-LTX}$ .

### Leaf area

The leaf area of the maize plants are presented in Figure 4.9. There was significant difference ( $P = 0.00$ ,  $N = 2$ ) between plants of different treatments, but no significant difference within treatments ( $P = 0.014$ ,  $N = 2$ ).

An increase in leaf area may be due to the application of NH<sub>4</sub>-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. Similarly results were obtained by Mahabir Singh and Rajodia (1989).

Table 4.8: Analysis of variance (ANOVA) of the leaf area of maize plant

		Sum of Squares	df	Mean Square	F	Sig
<b>Between treatments</b>		<b>4427401.139</b>	<b>17</b>	<b>260435.361</b>		
<b>Within Treatments</b>	<b>Between samples</b>	<b>758931.361</b>	<b>1</b>	<b>758931.361</b>	<b>56.365</b>	<b>0.000</b>
	<b>Non additivity</b>	<b>74257.926</b>	<b>1</b>	<b>74257.926</b>	<b>7.683</b>	<b>0.014</b>
	<b>Balance</b>	<b>154641.213</b>	<b>16</b>	<b>9665.076</b>		
	<b>Total</b>	<b>228899.139</b>	<b>17</b>	<b>13464.655</b>		
	<b>Total</b>	<b>987830.500</b>	<b>18</b>	<b>54879.472</b>		
<b>Total</b>		<b>5415231.639</b>	<b>35</b>	<b>154720.904</b>		

### Stem thicknes

There was significant difference between the samples treated with NH<sub>4</sub>LTX + Soil and samples with no NH<sub>4</sub>LTX ( $P = 0.000$ ,  $N = 2$ ) as well as between samples of the same treatments ( $P = 0.000$ ,  $N = 2$ ) as shown in Table 4.9.

Table 4.9: Analysis of variance (ANOVA) of the stem thickness of maize plants grown in LTX + Soil mixture and Soil only treatments

		Sum of Squares	df	Mean Square	F	Sig
Between treatments		3.509	53	0.066		
Within treatments	Between samples	0.697	1	0.697	156.992	0.000
	Residual	Non additivity	1	0.172	141.016	0.000
		Balance	52	0.001		
		Total	53	0.004		
	Total	0.932	54	0.017		
Total		4.442	107	0.042		

### Summary of results

The results for the maize plants that grew in the LTX + Soil treatment gave higher values for all the parameters investigated in the study, indicative of the positive effect the ammonium exchanged zeolite X had on the soil. This positive effect includes increase in porosity, infiltration rate and water retention capacity.



### 4.3.2 Growth parameters of okro plants

All data generated were analysed statistically with SPSS. The average values of the parameters investigated were compared based on the treatments, that is LTX + Soil substrate and Soil only substrate.

#### Plant height

There was significant difference between the samples treated with  $\text{NH}_4\text{LTX}$  + Soil and samples with no  $\text{NH}_4\text{LTX}$  ( $P = 0.000$ ,  $N = 2$ ) as well as between samples of the same treatments ( $P = 0.000$ ,  $N = 2$ ) as shown in Table 4.10. The development of the okro plants in height is shown in Figure 4.5.

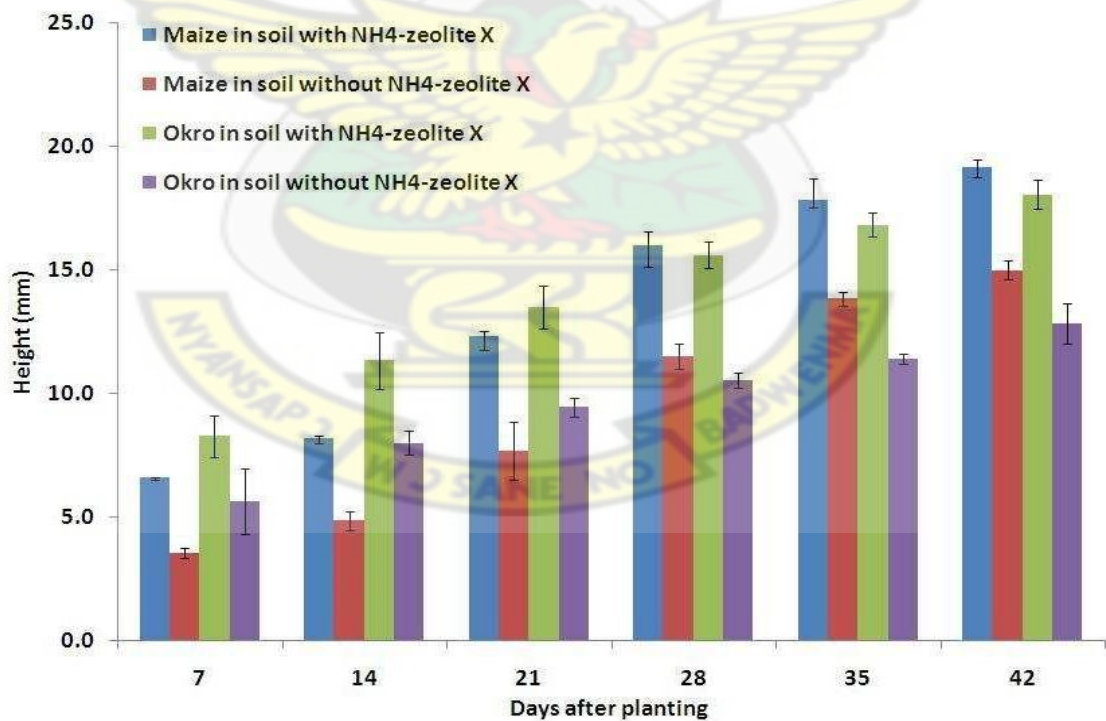


Figure 4.5: Average plant height of maize and okro plants grown in LTX + Soil mixture and Soil only treatments

Table 4.10: Analysis of variance (ANOVA) of the height of okro plants grown in LTX + Soil mixture and Soil only treatments

		Sum of Squares	df	Mean Square	F	Sig
<b>Between treatments</b>		<b>300.098</b>	<b>17</b>	<b>17.653</b>		
<b>Within treatments</b>	<b>Between samples</b>	<b>165.980</b>	<b>1</b>	<b>165.980</b>	<b>203.514</b>	<b>0.000</b>
	<b>Non additivity</b>	<b>9.135</b>	<b>1</b>	<b>9.135</b>	<b>30.903</b>	<b>0.000</b>
	<b>Balance</b>	<b>4.730</b>	<b>16</b>	<b>0.296</b>		
	<b>Total</b>	<b>13.865</b>	<b>17</b>	<b>0.816</b>		
<b>Total</b>		<b>479.943</b>	<b>35</b>	<b>13.713</b>		

### Number of leaves

The average number of leaves per okro plant, for three plants counted per treatment at six occasions during the trial, is shown in Figure 4.6. The LTX + 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 ( $N = 0.000$ ,  $N = 2$ ) as shown in Table 4.11.

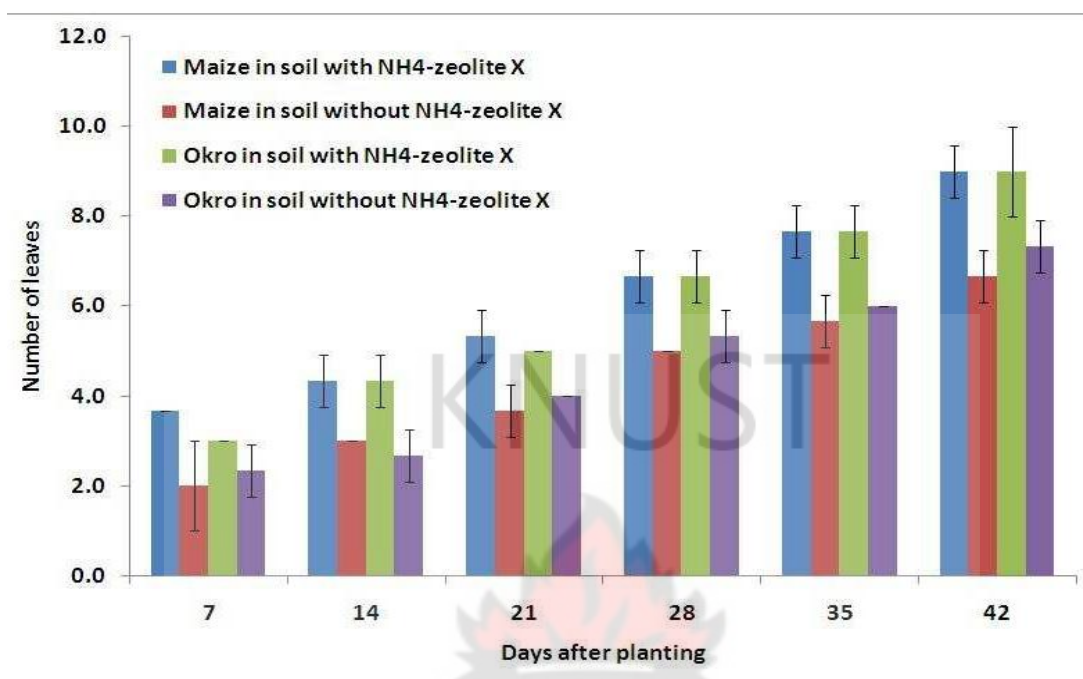


Figure 4.6: Average number of leaves of maize and okro plants grown in LTX + Soil mixture and Soil only treatments

Table 4.11: Analysis of variance (ANOVA) of the number of leaves of okro plants grown in LTX + Soil mixture and Soil only treatments

		Sum of Squares	df	Mean Square	F	Sig
<b>Between treatments</b>		<b>133.222</b>	<b>17</b>	<b>7.837</b>		
<b>Within treatments</b>	<b>Between samples</b>	<b>16.000</b>	<b>1</b>	<b>16.000</b>	<b>45.333</b>	<b>0.000</b>
	<b>Non additivity</b>	<b>0.654</b>	<b>1</b>	<b>0.654</b>	<b>1.957</b>	<b>0.181</b>
	<b>Balance</b>	<b>5.346</b>	<b>16</b>	<b>0.334</b>		
	<b>Total</b>	<b>6.000</b>	<b>17</b>	<b>0.353</b>		
	<b>Total</b>	<b>22.000</b>	<b>18</b>	<b>1.222</b>		
<b>Total</b>		<b>155.222</b>	<b>35</b>	<b>4.435</b>		

## Fresh weight

There was significant difference between the samples treated with  $\text{NH}_4\text{LTX}$  + Soil and samples with no  $\text{NH}_4\text{LTX}$  ( $P = 0.000$ ,  $N = 2$ ) as well as between samples of the same treatments ( $P = 0.000$ ,  $N = 2$ ) as shown in Table 4.9

Table 4.12: Analysis of variance (ANOVA) of the fresh (wet) weight of okro plants grown in LTX + Soil mixture and Soil only treatments

		Sum of Squares	df	Mean Square	F	Sig
Between treatments		17.835	17	1.049		
Within treatments	Between samples	14.478	1	14.478	54.943	0.000
	Non additivity	4.431	1	4.431	1452.117	0.000
	Balance	0.049	16	0.003		
	Total	4.480	17	0.264		
	Total	18.958	18	1.053		
Total		36.792	35	1.051		

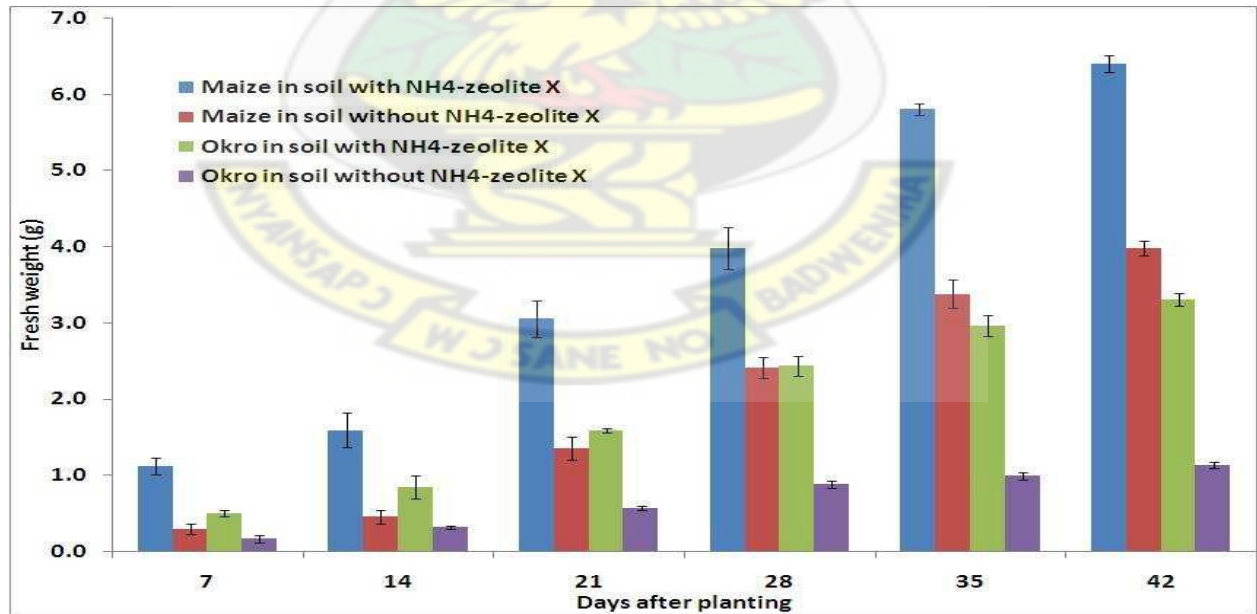


Figure 4.7: Average fresh (wet) weight of maize and okro plants grown in LTX + Soil mixture and Soil only treatments

## Dry weight

The dry weight of the okro plants are presented in Figure 4.8. There was significant difference between the samples treated with  $\text{NH}_4\text{LTX} + \text{Soil}$  and samples with no  $\text{NH}_4\text{LTX}$  ( $P = 0.000$ ,  $N = 2$ ) as well as between samples of the same treatments ( $P = 0.000$ ,  $N = 2$ ) as shown in Table 4.9. Table 4.13 is the ANOVA of dry weights of the maize plants for the two treatments.

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 %). This result is similar to that obtained by Leggo et al., (2006).

Table 4.13: Analysis of variance (ANOVA) of the dry weight of okro plant

		Sum of Squares	Df	Mean Square	F	Sig
<b>Between treatments</b>		<b>0.368</b>	<b>17</b>	<b>0.022</b>		
<b>Within treatments</b>	<b>Between samples</b>	<b>0.448</b>	<b>1</b>	<b>0.448</b>	<b>46.085</b>	<b>0.000</b>
	<b>Non additivity</b>	<b>0.163</b>	<b>1</b>	<b>0.163</b>	<b>1236.253</b>	<b>0.000</b>
	<b>Balance</b>	<b>0.002</b>	<b>16</b>	<b>0.000</b>		
	<b>Total</b>	<b>0.165</b>	<b>17</b>	<b>0.010</b>		
	<b>Total</b>	<b>0.613</b>	<b>18</b>	<b>0.034</b>		
<b>Total</b>		<b>0.981</b>	<b>35</b>	<b>0.028</b>		

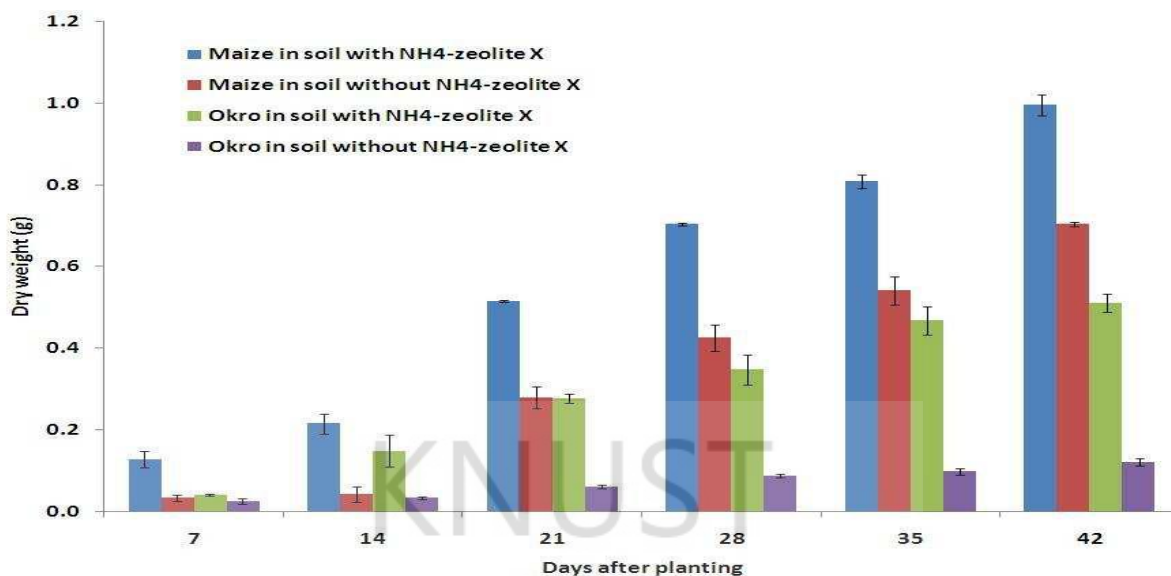


Figure 4.8: Average dry weight of maize and okro plants grown in LTX + Soil mixture and Soil only treatments

### Leaf area

The leaf area of the okro plants are presented in Figure 4.9. 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 LTX + Soil treatment with about 434 mm<sup>2</sup> 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 LTX + Soil treatment. The

ANOVA is given in Table 4.14

There was significant difference between the samples treated with NH<sub>4</sub>LTX + Soil and samples with no NH<sub>4</sub>LTX ( $P = 0.000$ ,  $N = 2$ ) as well as between samples of the same treatments ( $P = 0.000$ ,  $N = 2$ ). This may be due to the positive effect of NH<sub>4</sub>-LTX on cell division and cell elongation leading to enhanced leaf expansion. Shekhar (1974) also re-



ported similar results. Similarly, Dashora and Jain (1994) also reported an increased leaf area index due to the application of triacontanol in soybean.

Table 4.14: Analysis of variance (ANOVA) of the leaf area of okro plants grown in LTX + Soil mixture and Soil only treatments

		Sum of Squares	Df	Mean Square	F	Sig
<b>Between treatments</b>		<b>269027.806</b>	<b>17</b>	<b>15825.165</b>		
<b>Within treatments</b>	<b>Between samples</b>	<b>278960.028</b>	<b>1</b>	<b>278960.028</b>	<b>464.548</b>	<b>0.000</b>
	<b>Residual</b>	<b>7375.943</b>	<b>1</b>	<b>7375.943</b>	<b>41.664</b>	<b>0.000</b>
	<b>Non additivity</b>	<b>2832.529</b>	<b>16</b>	<b>177.033</b>		
	<b>Balance</b>	<b>10208.472</b>	<b>17</b>	<b>600.498</b>		
	<b>Total</b>	<b>289168.500</b>	<b>18</b>	<b>16064.917</b>		
<b>Total</b>		<b>558196.306</b>	<b>35</b>	<b>15948.466</b>		

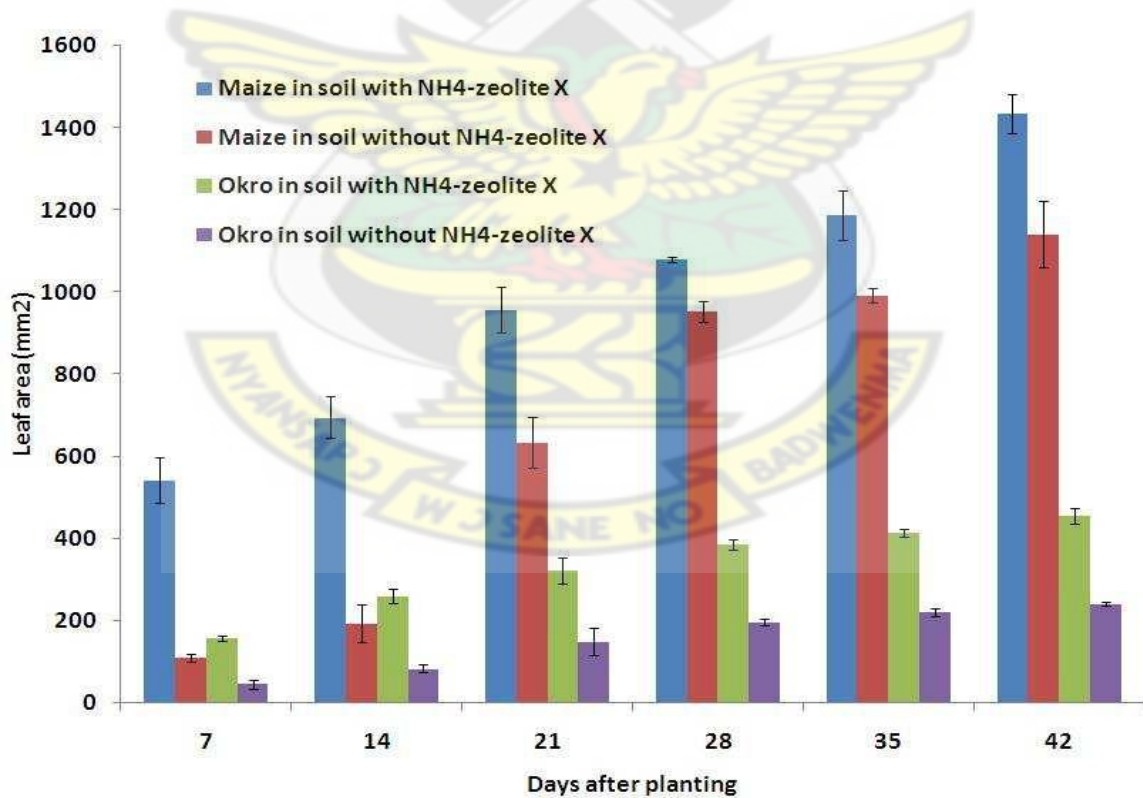


Figure 4.9: Average leaf area of maize and okro plants grown in LTX + Soil mixture and Soil only treatments

## Stem thickness

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 ( $P = 0.000$ ,  $N = 2$ ) as shown in Table 4.11. Soil recorded the highest values of stem thickness throughout the investigative period. This is illustrated in Figure 4.16.

Table 4.15: Analysis of variance (ANOVA) of the stem thickness of okro plants grown in LTX + Soil mixture and Soil only treatments

		Sum of Squares	Df	Mean Square	F	Sig
<b>Between treatments</b>		<b>1.565</b>	<b>53</b>	<b>0.030</b>		
<b>Within treatments</b>	<b>Between Items</b>	<b>0.131</b>	<b>1</b>	<b>0.131</b>	<b>162.829</b>	<b>0.000</b>
	<b>Residual</b>	<b>Non additivity</b>	<b>0.000</b>	<b>0.000</b>	<b>0.157</b>	<b>0.694</b>
		<b>Balance</b>	<b>0.042</b>	<b>0.001</b>		
		<b>Total</b>	<b>0.043</b>	<b>0.001</b>		
	<b>Total</b>	<b>0.173</b>	<b>54</b>	<b>0.003</b>		
<b>Total</b>		<b>1.738</b>	<b>107</b>	<b>0.016</b>		

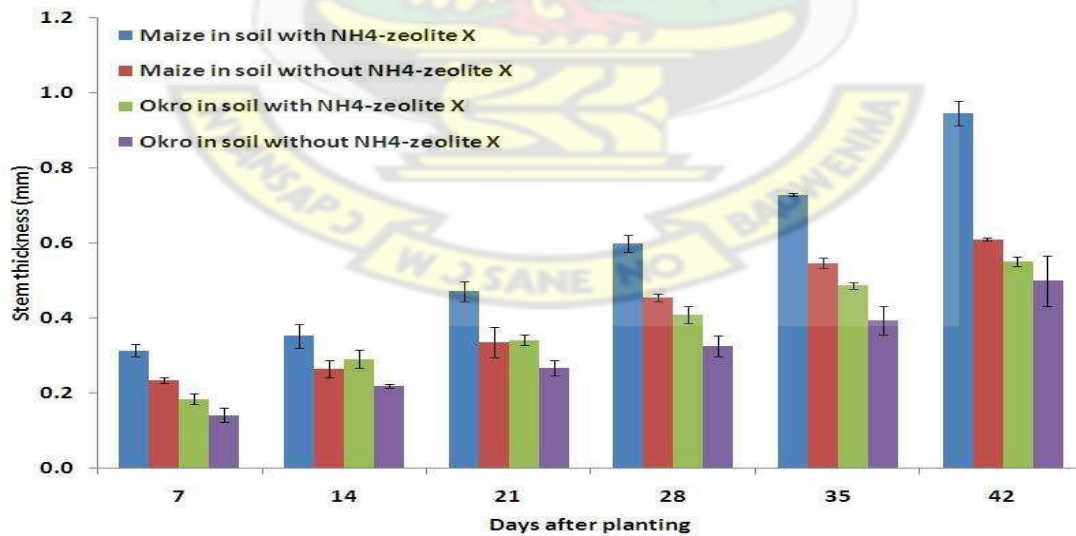


Figure 4.16: Average stem thickness of maize and okro plants grown in LTX + Soil mixture and Soil only treatment

## Summary of results

The results in total for the okro plants show that LTX + Soil treatment gives the largest plants. They have a faster development and get a higher fresh weight and dry weight and a larger leaf area. Germination occurred faster in the LTX + Soil treatment than it occurred in the Soil only treatment.

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## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 General conclusion

The investigation of the effect of ammonium exchanged Linde-type X zeolite ( $\text{NH}_4\text{-LTX}$ ), on maize and okro plants showed some increase in growth when  $\text{NH}_4\text{-LTX}$  was added to the soil. In both maize and okro, the growth increased with the application of 5 % w/w  $\text{NH}_4\text{-LTX}$  to soil of low nutrients. The results indicated that  $\text{NH}_4\text{-LTX}$  has an effect on the growth medium of maize and okro plants. The most important factor is probably that  $\text{NH}_4\text{-LTX}$  increased the supply of nutrients to the plants.  $\text{NH}_4\text{-LTX}$  ability to retain moisture could also have affected the growth of the plants positively.  $\text{NH}_4\text{-LTX}$  might have prevented water from draining out from the pots and thereby giving the plants access to more moisture for a longer time. These conclusions support those of Hsu et al., who found an increase in the effect of zeolite additions to soil when the clay content of the soil decreased.

The structure and chemical composition of the soil was also altered by the addition of  $\text{NH}_4\text{-LTX}$ . The porous structure of zeolite might have improved the aeration and created a better structure which could enhance root growth and benefited the plant.

$\text{NH}_4\text{-LTX}$  increase germination rates. This could be observed in this trial. Plants grown in  $\text{LTX} + \text{Soil}$  treatment sprouted first before those in the soil only treatment. Seeds used were purchase from the Food and Agriculture Organizations (FAO) stores in Kumasi. Seeds obtained had little or no genetic variation. Other external factors such as very high temperature and flooding that could contribute to uneven germination were eliminated. Fur-

thermore, all pots were watered thoroughly at the beginning of the trial with equal amounts of water. This may have given the plants the same prerequisites during the germination period.

The trial results show that  $\text{NH}_4\text{-LTX}$  substrate can achieve similar results as conventionally produced plants fertilizers. However, to be able to evaluate this in a better way, a treatment with some kind of fertilization could be included in the trial in order to compare the effect of  $\text{NH}_4\text{-LTX}$  to another nutrient source.

Moreover, LTX acts as slow-release fertilizer in a process combining dissolution and ion exchange reactions. However, the long-term effect of a slow-release fertilizer could not be explored in this trial. A longer time would be needed to investigate this process.

This study was intended to establish the efficacy of  $\text{NH}_4\text{-LTX}$  as a soil amendment and also as a source of nutrients for plants.

## **5.2 Recommendations**

From literature it can be concluded that zeolites have a huge potential in many areas of application including the horticultural sector. However, there are many factors to be taken into consideration when synthesizing zeolite for horticulture applications. These factors include physical and chemical properties of the different types of zeolites, the pH, physical and chemical properties of the soil.

High yield is the main parameter considered when dealing with food crops, but it is not automatically connected to increased growth. Hence the yield is the best measurement of  $\text{NH}_4\text{-LTX}$  effectiveness. Therefore a longer time would be needed to investigate this process.

Crops with longer cultural programmed are also needed to see the effect of  $\text{NH}_4\text{-LTX}$  as a slow-release fertilizer and to be able to decide the optimum concentration of  $\text{NH}_4\text{-LTX}$  needed to be applied to the soil.

As stated, an experiment comparing conventional fertilizer and  $\text{NH}_4\text{-LTX}$  could be investigated. Also, the type of soil needed to mix  $\text{NH}_4\text{-LTX}$  with is another area which needs to be explored. Zeolite is alkaline in nature and would be more suitable for acidic soils, nevertheless, it would be interesting to examine other possibilities.

To gain more knowledge about nutrient uptake, the level of nutrition in the plants could be analyzed at various levels during a trial in which case destructive analysis cannot be used to determine growth parameters. Zeolites help retain the nutrients in the root zone, this could lead to more effective use of nutrients by the plant and a corresponding increase in yield.

The economic potential and profitable can be fully harnessed if  $\text{NH}_4\text{-LTX}$  is synthesized with local materials like rice husk, plantain peels, cocoa pods and bauxite. Ashes from plantain peels and cocoa pods are rich in potassium, whereas ashes of rice husk are rich in silicate and bauxite is composed of alumina.



## REFERENCES

- Adams, F. (1971). Ionic concentrations and activities in soil solutions. *Soil Science Society of America Proceedings* **35**: 420 – 426
- Akhtaruzzaman, M. A., (1998). Influence of rates of nitrogen and phosphorus fertilizers on the productivity of mungbean. Ph.D. Thesis. Institute of Postgraduate Studies in Agriculture, Gazipur, India.
- Auerbach, S. M., Carrado, K. A., and Dutta, P. K. (2003). Handbook of zeolite science and technology, CRC Press, London, New York. 535
- Agbede, T. M., Ojeniyi, S. O. and Awodun, M. A. (2008). Effect of Tillage Method on Growth, Grain Yield and Nutrient Content of Sorghum (*Sorghum bicolor L.*) in Forest Savanna Transition Zone of Nigeria. *International Journal of Sustainable Crop Production* **3**(5): 35-39.
- Burriesci, N., Valente, S., Ottana, R., Cimino, G. and Zipelli, C. (1984). Utilization of Zeolites in spinach growing. *Zeolites* **4**: 5 - 8.
- Beiersdorfer, R. E., Ming, D. W., and Galindo Jr., C., (2003). Solubility and cation exchange properties of zeoponic substrates. *Microporous and Mesoporous Materials* **61**: 231–247.
- Brady, N. C., and Weil, R. R. (2002). The nature and properties of soils. 13th ed. Upper Saddle River, New Jersey, NJ: Prentice Hall; 960

Breck, D. W. (1964). Crystalline molecular sieves. *Journal of Chemical Education* **41**: 678-689.

Breck, D. W. (1971). Recent advance in zeolite science. *American chemical society*. 1-19.

Breck, D. W. (1974). Zeolite Molecular Sieves: structure, chemistry and use. Canada: John Wiley and Sons Ltd.

Breck, D. W. and Flanigen, E. M. (1964). Synthesis and properties of Union Carbide zeolites L, X and Y. USA: Union Carbide Corporation.

Buckmann, H. O., and Brady, N. C. (1969). The nature and properties of soil, (the Macmillan Company, London).1-39, 137-163, 422-483, 503-515.

Dashora, L. D. and Jain, P. M., (1994). Effect of growth regulators and phosphorus level on growth and yield of soybean. *Madras Agricultural Journal* **81**(5): 235-237.

Dondur, V., Raki, V., Damjanovi, L. and Auroux, A. (2005). Comparative study of the active sites in zeolites by different probe molecules. *Journal of Serbia Chemical Society* **70**: 457-474.

Elliot, A. D. and Zhang, D. (2005). Controlled Release Zeolite Fertilizers: A Value Added Product Produced from Fly Ash, World of Coal Ash (WOCA), Lexington, Kentucky, USA.

Fansuri, H., Pritchard, D. and Zhang, D. (2008). Manufacture of Low-Grade Zeolites from Fly Ash for Fertiliser Applications, Research Report 91, Cooperative Research Centre for Coal in Sustainable Development, Australia.

Ferdous, A. K. M., (2001). Effects of nitrogen and phosphorus fertilizers on nutrient uptake and productivity of edible podded pea. M.Sc. Thesis, Department of Agronomy, BSMRAU. Salna, Gazipur; 29-30.

Flanigen, M. and Mumpton, F. A. (1981). Commercial properties of natural zeolites. In: F.A. Mumpton (ed.). Mineralogy and geology of natural zeolites, Reviews in Mineralogy. *Mineral society of America* **4**: 165-175.

Gruener, J. E., Ming, D. W., Henderson, K. E., and Galindo Jr., C., (2003). Common ion effects in zeoponic substrates: wheat plant growth experiment. *Microporous and Mesoporous Materials* **61**: 223–230.

Hubicki, Z., Zieba, E., Wojcik, G. and Ryczkowski, J. (2008). FT-IR/PAS and SEM EDX Studies on Aluminosilicates modified by CS(I), TH(IV) and U(VI). *Molecular and Quantum Acoustics* **29**: 109-114

Hideo, M. (1968). Characteristics and Uses of Natural Zeolites. *Koatsugasu* **5**: 536-547.

Hsu, S. C., Wang, S. T., and Lin, T. H., (1967). Effect of Soil Conditioner on Taiwan Soils. Effects of Zeolite on Physio-Chemical Properties of Soils. *Journey of Taiwan Agriculture* **16**: 50-57

Huang, Z. T. and Petrovic, A. M. (1994). Clinoptilolite zeolite influence on nitrate leaching and nitrogen use efficiency in simulated and based golf greens. *Journal of Environmental Quality* **23**: 1190-1194

Kwakye-Awuah, B., Kenward, M. A., Williams, C. and Radecka, I. (2008). Antimicrobial action and efficiency of silver-loaded zeolite X. *Journal of Applied Microbiology* **104**: 1516-1524.

Khan MS, Zaidi A, Wani, P. A, Ahemad M, and Oves, M. (2009). Functional diversity among plant growth-promoting rhizobacteria. In: Khan MS, Zaidi A, Musarrat J (eds), *Microbial Strategies for Crop Improvement*, Springer, Berlin. 105-132.

Leggo, P. J., Ledesert, B., and Graham, C. (2006). The role of clinoptilolite in organo-zeolitic-soil systems used for Phytoremediation. *Science of the Total Environment* **363**: 1 – 10

Marx, E. S. (1999). Soil test interpretation guide, EC 1478. Oregon State University, Corvallis

Ming, D. W., and Allen, E. R., (2001). Use of natural zeolites in agronomy, horticulture, and environmental soil remediation. In: Bish, D., Ming, D. W., (Eds.), *Natural Zeolites: Occurrence, Properties, Applications. Reviews in Mineralogy & Geochemistry. Mineralogical Society of America, Washington, DC* **45**: 619–654.

Mühlbachová, G. and Šimon, T. (2003). Effects of zeolite amendment on microbial biomass and respiratory activity in heavy metal contaminated soils. *Plant, Soil and Environment* **49**: 536–541.

Mumpton F. A. (1999). La roca: Uses of Natural zeolites in agriculture and industry. *Geology, Mineralogy and Human Welfare* **96**: 3463-3470.

Mumpton, F. A. and Fishman, P. H. (1977). The Application of Natural Zeolites in Animal Science and Aquiculture. *Journal of Animal Science* **45**: 1188-1203

Naik, L. P. (1989). Studies on the effect of plant spacing and graded level of nitrogen, phosphorus and potassium on the yield and yield components of mid season garden pea (*Pisum sativum* L.) *Indian Journal of Horticulture* **46**: 234 - 239.

Nizam Nik Malek, N. A. (2007). Surfactant Modified Zeolite Y as a Sorbent for some Chromium and Arsenic Species in Water. Master of Science thesis. Universiti Teknologi, Malaysia.

Newsam, J. M. (1986). The zeolite cage structure, *Science*. 231; 1093-1099

Notario del Pino, J. S., Arteaga Padron, I. J., Gonzalez Martin, M. M. and Garcia Hernandez, J. E. (1994), Response of alfalfa to a phillipsite- based slow-release fertilizer. *Communication in Soil Science and Plant Analysis* **25**: 2231–2245.

Pansini, M. (1996). Natural zeolites as cation exchangers for environmental protection. *Mineralium deposita* **31**: 563-575.

Polat, E., Karaca, M., Demir, H., and Onus, A. N. (2004). Use of natural zeolite (clinoptilolite) in agriculture. *Journal of Fruit and Ornamental Plant Research*, Special edition **12**: 183-189

Ramesh, P., N.R. Panwar, Singh A. B., and Ramana, S. (2010). Effect of organic manures on productivity, nutrient uptake and soil fertility of maize-linseed cropping system. *Indian Journal of Agricultural Science* **78**: 351-354.

Şen, Ý. (2003). Spectroscopic Determination of Major Nutrients (N, P, K) of Soil. A Dissertation submitted to the Graduate School, Ýzmir Institute of Technology, Ýzmir, Turkey.

Singh, M. and Rajodia, R. B. (1989). Effect of gibberellic acid on growth and yield attributes of radish varieties. *Indian Journal of Plant Physiology*. 167-171.

Shekhar, V. C. (1974). Effect of nitrogen on growth and yield components of two cultivars of onion (*Allium cepa* L.). M. Sc. (Agric.) Thesis, University of Agricultural Sciences, Dharwad.

Troeh, F.R. and Thompson, L. M. (1993). Soils and Soil Fertility, (Oxford University Press Inc., New York). 3-15, 193-253.

Torii, K. (1978). Natural Zeolites: Occurrence, Properties, Use, eds. Sand, L. B. and Mumpton, F. A. (Pergamon, Elmsford, NY). 441- 450.



Voroney, R. P. and van Straaten, P. (1988). Use of natural zeolites in sand root zones for putting greens. *Greenmaster Magazine*. **8**.

Wallace, A. (1998). Some living plants and some additional products useful as soil conditioners and in various technologies. V. Zeolites and related substances. In *Handbook of Soil Conditioners* (eds Wallace, A. and Terry, R. E.), Marcel Dekker, Inc., New York. 477–479.

Xiubin, H., and Zhanbin, H. (2001). Zeolite application for enhancing water infiltration and retention in loess soil. *Resources, Conservation and Recycling* **34**: 45–52.

Yasuda, H., Takuma, K., Fukuda, T., Araki, Y., Suzuka, J. and Fukushima, Y. (1998). Effect of zeolite on water and salt control in soil. *Bulletin of the Institute of Tropical Agriculture, Kyushu University* **51**: 35 – 42.

Yang, S., Navrotsky, A. and Wilkin, R. (2001). Thermodynamics of ion exchanged and natural clinoptilolite. *American Mineralogist* **86**: 438 – 447.

Zelazny, L. W. and Calhoun, F. G. (1977). Palygorskite (attapulgite), sepiolite, talc, pyrophyllite and zeolites. In *Minerals in Soil Environments* (eds Dixon, J. B. and Weed, S. B.). *Soil Science Society of America, Madison WI*. 435–470.

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## Appendix

### 1. Development of maize plants

1.1 Descriptive statistics of stem thickness of maize plant grown in LTX + Soil treatment and Soil only treatment.

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
stem thickness of maize in LTX + Soil	7	1	0.320000	.	.	.	.	0.3200	0.3200
	14	1	0.388000	.	.	.	.	0.3880	0.3880
	21	1	0.487000	.	.	.	.	0.4870	0.4870
	28	1	0.611000	.	.	.	.	0.6110	0.6110
	35	1	0.764000	.	.	.	.	0.7640	0.7640
	42	1	0.981000	.	.	.	.	0.9810	0.9810
	Total	6	0.591833	.2481495	.1013066	.331416	.852250	0.3200	0.9810
stem thickness of maize in Soil only	7	1	0.245000	.	.	.	.	0.2450	0.2450
	14	1	0.271000	.	.	.	.	0.2710	0.2710
	21	1	0.319000	.	.	.	.	0.3190	0.3190
	28	1	0.486000	.	.	.	.	0.4860	0.4860
	35	1	0.571000	.	.	.	.	0.5710	0.5710
	42	1	0.593000	.	.	.	.	0.5930	0.5930
	Total	6	0.414167	.1548605	0.0632215	0.251651	0.576683	0.2450	0.5930

1.2 Descriptive statistics of stem length (plant height) of maize plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Interval for Mean			
						Lower Bound	Upper Bound		
stem length (cm) of maize in LTX + soil	7.00	1	6.7000					6.70	6.70
	14.00	1	8.4000					8.40	8.40
	21.00	1	13.0000					13.00	13.00
	28.00	1	15.0000					15.00	15.00
	35.00	1	17.5000					17.50	17.50
	42.00	1	18.8000					18.80	18.80
	Total	6	13.2333	4.86648	1.98673	8.1263	18.3404	6.70	18.80
stem length (cm) of maize in soil only	7.00	1	3.3000					3.30	3.30
	14.00	1	4.4000					4.40	4.40
	21.00	1	9.0000					9.00	9.00
	28.00	1	12.0000					12.00	12.00
	35.00	1	14.0000					14.00	14.00
	42.00	1	14.7000					14.70	14.70
	Total	6	9.5667	4.86237	1.98506	4.4639	14.6694	3.30	14.70

1.3 Descriptive statistics of number of leaf of maize plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
number of leaves of maize plant in LTX + Soil	7	1	4.0000	.	.	.	.	4.00	4.00
	14	1	5.0000	.	.	.	.	5.00	5.00
	21	1	5.0000	.	.	.	.	5.00	5.00
	28	1	7.0000	.	.	.	.	7.00	7.00
	35	1	8.0000	.	.	.	.	8.00	8.00
	42	1	10.0000	.	.	.	.	10.00	10.00
	Total	6	6.5000	2.25832	.92195	4.1300	8.8700	4.00	10.00
number of leaves of maize in Soil only	7	1	3.0000	.	.	.	.	3.00	3.00
	14	1	3.0000	.	.	.	.	3.00	3.00
	21	1	4.0000	.	.	.	.	4.00	4.00
	28	1	5.0000	.	.	.	.	5.00	5.00
	35	1	6.0000	.	.	.	.	6.00	6.00
	42	1	7.0000	.	.	.	.	7.00	7.00
	Total	6	4.6667	1.63299	.66667	2.9529	6.3804	3.00	7.00

1.4 Descriptive statistics of fresh weight (wet weight) of maize plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
fresh weight of maize plant in Soil only	7	1	0.355000	.	.	.	.	0.3550	0.3550
	14	1	0.551000	.	.	.	.	0.5510	0.5510
	21	1	1.026000	.	.	.	.	1.0260	1.0260
	28	1	2.533000	.	.	.	.	2.5330	2.5330
	35	1	3.164000	.	.	.	.	3.1640	3.1640
	42	1	3.924000	.	.	.	.	3.9240	3.9240
	Total	6	1.925500	1.4873978	.6072276	0.364572	3.486428	.3550	3.9240
fresh weight of maize plant in LTX + Soil	7	1	1.215000	.	.	.	.	1.2150	1.2150
	14	1	1.667000	.	.	.	.	1.6670	1.6670
	21	1	1.929000	.	.	.	.	1.9290	1.9290
	28	1	3.513000	.	.	.	.	3.5130	3.5130
	35	1	5.879000	.	.	.	.	5.8790	5.8790
	42	1	6.281000	.	.	.	.	6.2810	6.2810
	Total	6	3.414000	2.2090066	0.9018232	1.095790	5.732210	1.2150	6.2810

1.5 Descriptive statistics of dry weight of maize plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
dry weight (g) of maize in LTX + soil	7.00	1	0.104400					0.1044	0.1044
	14.00	1	0.238400					0.2384	0.2384
	21.00	1	0.516800					0.5168	0.5168
	28.00	1	0.704100					0.7041	0.7041
	35.00	1	0.827200					0.8272	0.8272
	42.00	1	0.971200					0.9712	0.9712
	Total	6	0.560350	0.3388538	0.1383365	0.204745	0.915955	0.1044	0.9712
dry weight (g) of maize in soil only	7.00	1	0.036000					0.0360	0.0360
	14.00	1	0.063300					0.0633	0.0633
	21.00	1	0.293100					0.2931	0.2931
	28.00	1	0.462000					0.4620	0.4620
	35.00	1	0.501200					0.5012	0.5012
	42.00	1	0.708100					0.7081	0.7081
	Total	6	0.343950	0.2636103	0.1076185	0.067308	0.620592	0.0360	0.7081



1.6 Descriptive statistics of leaf area in square milimeter of maize plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
leaf area of maize in LTX + Soil	7	1	384.0000	.	.	.	.	384.00	384.00
	14	1	646.0000	.	.	.	.	646.00	646.00
	21	1	1021.0000	.	.	.	.	1021.00	1021.00
	28	1	1086.0000	.	.	.	.	1086.00	1086.00
	35	1	1124.0000	.	.	.	.	1124.00	1124.00
	42	1	1471.0000	.	.	.	.	1471.00	1471.00
	Total	6	955.3333	384.14980	156.82850	552.1928	1358.4738	384.00	1471.00
leaf area of maize plant in Soil only	7	1	106.0000	.	.	.	.	106.00	106.00
	14	1	244.0000	.	.	.	.	244.00	244.00
	21	1	564.0000	.	.	.	.	564.00	564.00
	28	1	929.0000	.	.	.	.	929.00	929.00
	35	1	1008.0000	.	.	.	.	1008.00	1008.00
	42	1	1047.0000	.	.	.	.	1047.00	1047.00
	Total	6	649.6667	407.86795	166.51139	221.6355	1077.6978	106.00	1047.00

## 2. Development of okro plants

### 2.1 Descriptive statistics of stem thickness of okro plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Inter- val for Mean		Minimum	Maximum
						Lower	Upper		
						Bound	Bound		
stem thick- ness of okro in LTX+soil	7.00	1	0.163000					0.1630	0.1630
	14.00	1	0.287000					0.2870	0.2870
	21.00	1	0.305000					0.3050	0.3050
	28.00	1	0.408000					0.4080	0.4080
	35.00	1	0.482000					0.4820	0.4820
	42.00	1	0.538000					0.5380	0.5380
	Total	6	0.363833	0.1385257	0.0565529	0.218460	0.509207	0.1630	0.5380
stem thick- ness of okro in soil only	7.00	1	0.139000					0.1390	0.1390
	14.00	1	0.208000					0.2080	0.2080
	21.00	1	0.247000					0.2470	0.2470
	28.00	1	0.305000					0.3050	0.3050
	35.00	1	0.352000					0.3520	0.3520
	42.00	1	0.421000					0.4210	0.4210
	Total	6	0.278667	0.1018168	0.0415665	0.171816	0.385517	0.1390	0.4210

2.2 Descriptive statistics of stem length (plant height) of okro plant grown in LTX + Soil treatment and Soil only treatment

						95% Confidence Interval for Mean			
		N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
stem length (cm) of okro in LTX + soil	7.00	1	7.4000					7.40	7.40
	14.00	1	12.0000					12.00	12.00
	21.00	1	14.0000					14.00	14.00
	28.00	1	15.0000					15.00	15.00
	35.00	1	16.3000					16.30	16.30
	42.00	1	17.5000					17.50	17.50
	Total	6	13.7000	3.62105	1.47829	9.8999	17.5001	7.40	17.50
stem length (cm) of okro in soil only	7.00	1	6.2000					6.20	6.20
	14.00	1	8.5000					8.50	8.50
	21.00	1	9.5000					9.50	9.50
	28.00	1	10.6000					10.60	10.60
	35.00	1	11.6000					11.60	11.60
	42.00	1	12.0000					12.00	12.00
	Total	6	9.7333	2.16487	.88380	7.4614	12.0052	6.20	12.00

2.3 Descriptive statistics of number of leaf of okro plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval		Minimum	Maximum
						for Mean			
						Lower Bound	Upper Bound		
number of leaves of okro in LTX + soil	7.00	1	3.0000					3.00	3.00
	14.00	1	5.0000					5.00	5.00
	21.00	1	5.0000					5.00	5.00
	28.00	1	7.0000					7.00	7.00
	35.00	1	7.0000					7.00	7.00
	42.00	1	10.0000					10.00	10.00
	Total	6	6.1667	2.40139	0.98036	3.6466	8.6868	3.00	10.00
number of leaves of okro in soil only	7.00	1	3.0000					3.00	3.00
	14.00	1	3.0000					3.00	3.00
	21.00	1	4.0000					4.00	4.00
	28.00	1	5.0000					5.00	5.00
	35.00	1	6.0000					6.00	6.00
	42.00	1	7.0000					7.00	7.00
	Total	6	4.6667	1.63299	0.66667	2.9529	6.3804	3.00	7.00

2.4 Descriptive statistics of fresh weight (wet weight) of okro plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
wet weight of okro in LTX + soil	7.00	1	0.535000					0.5350	0.5350
	14.00	1	0.906000					0.9060	0.9060
	21.00	1	1.577000					1.5770	1.5770
	28.00	1	2.397000					2.3970	2.3970
	35.00	1	2.842000					2.8420	2.8420
	42.00	1	3.206000					3.2060	3.2060
	Total	6	1.910500	1.0765628	.4395049	.780717	3.040283	0.5350	3.2060
wet weight of okro in soil only	7.00	1	0.219000					0.2190	0.2190
	14.00	1	0.312000					0.3120	0.3120
	21.00	1	0.598000					0.5980	0.5980
	28.00	1	0.829000					0.8290	0.8290
	35.00	1	0.935000					0.9350	0.9350
	42.00	1	1.081000					1.0810	1.0810
	Total	6	0.662333	0.3466478	0.1415184	0.298549	1.026118	0.2190	1.0810

2.5 Descriptive statistics of dry weight of okro plant grown in LTX + Soil treatment and Soil only treatment

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
dry weight(g) of okro in LTX + soil	7.00	1	0.043300					0.0433	0.0433
	14.00	1	0.093600					0.0936	0.0936
	21.00	1	0.283400					0.2834	0.2834
	28.00	1	0.328300					0.3283	0.3283
	35.00	1	0.496600					0.4966	0.4966
	42.00	1	0.483700					0.4837	0.4837
	Total	6	0.288150	0.1903297	0.0777018	0.088411	0.487889	0.0433	0.4966
dry weight(g) of okro in soil only	7.00	1	0.027400					0.0274	0.0274
	14.00	1	0.035100					0.0351	0.0351
	21.00	1	0.064700					0.0647	0.0647
	28.00	1	0.082400					0.0824	0.0824
	35.00	1	0.097600					0.0976	0.0976
	42.00	1	0.123400					0.1234	0.1234
	Total	6	0.071767	0.0369032	0.0150656	0.033039	0.110494	0.0274	0.1234



2.6 Descriptive statistics of leaf area in square milimeter of okro plant grown in LTX + Soil treatment and Soil only treatment

						95% Confidence Interval for Mean			
		N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
leaf area (sqr mm) of okro in LTX + soil	7.00	1	162.000000	.	.	.	.	162.0000	162.0000
	14.00	1	277.000000	.	.	.	.	277.0000	277.0000
	21.00	1	313.000000	.	.	.	.	313.0000	313.0000
	28.00	1	372.000000	.	.	.	.	372.0000	372.0000
	35.00	1	402.000000	.	.	.	.	402.0000	402.0000
	42.00	1	434.000000	.	.	.	.	434.0000	434.0000
	Total	6	326.666667	99.0144771	40.4224910	222.757346	430.575988	162.0000	434.0000
leaf area (sqr mm) of okro in soil only	7.00	1	58.000000	.	.	.	.	58.0000	58.0000
	14.00	1	74.000000	.	.	.	.	74.0000	74.0000
	21.00	1	159.000000	.	.	.	.	159.0000	159.0000
	28.00	1	187.000000	.	.	.	.	187.0000	187.0000
	35.00	1	212.000000	.	.	.	.	212.0000	212.0000
	42.00	1	241.000000	.	.	.	.	241.0000	241.0000
	Total	6	155.166667	74.3704690	30.3616169	77.119646	233.213687	58.0000	241.0000