Synthesis and characterization of water soluble Zn-NPK fertilizer

S. A. Amolegbe[1*], S. Adewuyi[1], C. A. Akinremi[1] S. Peter[1], J.A. Azeez[2]

[1]Department of Chemistry, College of Physical Sciences, Federal University of Agriculture, Abeokuta, Ogun State
[2]Department of Soil Science and Land Management, College of Plant Sciences, Federal University of Agriculture, Abeokuta, Ogun State

*Corresponding Author: e-mail: amolegbesa@funaab.edu.ng

Abstract

The fertilizer complex $K[Zn(CO(NH_2)_2(PO_4)]$ was prepared by direct combination reaction under thermal condition. Characterization of the Zn-N-P-K with elemental analysis, FT-IR spectroscopy and electrical conductivity fit well for the expected properties of the metal based fertilizer. From the elemental analysis, Zn: N: P: K micronutrient fertilizer (7.34%, 7.41%, 6.91% and 6.97%) are in (1: 1:1:1) good proportion for plant growth. The electrical conductivity test shows the population or mobility of ions with Zn-NPK (electrolyte) >NPK. Meanwhile, the bathochromic shifts of 513, 3406 & 1643 cm^{-1} in Fe-C, (NH_2) & CO functional groups of the metal based fertilizer confirms the coordination activity of the organic fertilizer.

Keywords: coordination compounds, fertilizer, metal-based fertilizer, FT-IR spectroscopy, conductivity.

1. Introduction

One of the most common fertilizer is NPK comprised primarily of the three primary nutrients required for healthy plant growth. The agriculture industry relies heavily on the use of NPK fertilizer to accomplish global food supply and ensure healthy crops (Chien, *et al.,* 2017). There are numerous building blocks of life that plants need for healthy and optimum growth. Without these nutrients, plants cannot grow to their full potential, will provide lower yields, and be more prone to diseases (Dobermann, *et al.,* 2005). The three most important nutrients, without any one of which plants could not survive, are referred to as the primary macronutrients: Nitrogen (N), Phosphorus (P), and Potassium (K). Soils often lack these nutrients, either naturally, as a result of over cultivation or other environmental factors. In cases where soils are lacking, nutrients must apply to the soil in order to create the ideal environment for optimal plant growth. The functions of the macronutrients include: Nitrogen (N): formation of chlorophyll, Phosphorus (P); development of roots, flowers, seeds, fruits: Potassium (K): cell formation, synthesis of carbohydrate and activation of various plant enzymes reactions (Garret, *et al.,* 2014). Fertilizers are classified in several ways. This is according to whether they produce a single nutrient which is called straight fertilizer or more than one nutrient called multi nutrient fertilizers. The overall percentages of NPK fertilizer are usually stated on the container. The grade designation is %N-%P_2O_5-%K_2O.It is commonly called NPK value. Usually, three numbers are used when giving the grade of a fertilizer product, and these three numbers always refer in order to the content of the primary nutrients: nitrogen, phosphorus, and potassium (NPK). If other nutrients are present, their content can also be indicated in the grade of the fertilizer product; each extra number is followed by the chemical symbol of the nutrient.12-6-22-2MgO is guaranteed by the manufacturer to contain: 12% N, 6%P,2% K_2O, and 2% MgO. The value is an elemental percentage only in the case of nitrogen, while phosphorus and potassium are expressed as oxides. Thus an NPK value of 6-24-12 means that 6% by weight is elemental nitrogen, 24% is phosphorus pentoxide and 12% is potash (National Code of Practice for Fertilizer Description and Labelling (Bodelier, *et al.,* 2017)

Apart from the macronutrients, plants require some other nutrients in small amount and they are called micronutrient like iron, manganese, copper, zinc etc. Zinc is a transition metal which is found in group 12 (IIB) of the periodic table first roll of the transition series. It has symbol as Zn and atomic number of thirty (30) and is very useful to plants and animals. Zinc is necessary for the carbohydrates, protein synthesis and the biosynthesis of the growth hormones in plant (Motalvo, D, 2016). The deficiency of Zinc in the soil can lead to poor leaf formation. The Presence of salt as micronutrient supplement to NPK fertilizer has been separately made available to soil. But there has not been a case of having it as an integral part of NPK as a single kit. Hence, this research work is aimed at synthesizing a new product of water soluble Zn-N-P-K complex fertilizer to improve soil nutrients for plants uptake.

2.0 METHODOLOGY

All reagents were of analytical grade and used without further purification. Infrared studies of synthesized Schiff base and metal complexes were recorded on a Shimadzu FT-IR Spectrophotometer in the 4000 - 350 cm^{-1} region. The conductivity measurement of the compounds were determined using the Fischer-John melting point apparatus.

2.1 Synthetic methods of Zn-N-P-K fertilizers

2.1.1 Reaction method one (1) (without KOH)

A method similar to previously reported was used with slight change (Benton J., 2012). The 20 mL of distilled water was used to dissolve 11.5 g of Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) in a beaker. The beaker was placed on a magnetic stirrer for stirring and heating for about three (3) minutes after complete dissolution of ammonium dihydrogen phosphate. 0.287 g of Zinc sulphate heptahydate ($ZnSO_4.7H_2O$) that has been dissolved with 20 mL of distilled water was added step-wisely to ammonium dihydrogen phosphate that has been already placed on the magnetic stirrer, stirring and heating were taken place simultaneously for another four minutes ,a white solution was formed. Dissolved 7.45 g with 20 mL of distilled water was also added to the mixture step-wisely after another four minutes 0.6g solution of urea (20 mL of distilled water was used for dissolution) was also reacted step-wisely with the mixture placed on the magnetic stirrer after another four minutes and the stirring and heating were not stopped. At exactly 90 ^{0}C a product was formed and the reaction was terminated by removing it from the magnetic stirrer and was allowed to cool. The percentage yield was calculated as 65%.

The chemical reaction steps of the first procedure

$$NH_4H_2PO_4 + ZnSO_4.7H_2O \longrightarrow NH_4ZnPO_4 + H_2SO_4 + 7H_2O$$

$$NH_4ZnPO_4 + KCl \longrightarrow KZnPO_4 + NH_4Cl$$

$$KZnPO_4 + CO(NH_2) \xrightarrow[90^oC]{} [K(CO(NH_2)_2Zn]PO_4$$

2.1.2 Reaction method two (2)(with KOH)

The reaction was carried out as was done in reaction method one but the number of mole used to calculate the macronutrients and micronutrient compounds was changed to 0.01mole instead of 0.1mole used to calculate the masses of macronutrients compounds and 0.001 mole was used to calculate the mass of micronutrient compound in step one (Shriver and Atkins, 2017). The temperature was not allowed to increase hence was maintained at 90^{0}C with the aid of a magnetic stirrer but after 20 minutes of heating 1 mL of KOH was added to reduce the acidity. The heating continued after the addition of KOH until the dryness was done to the extent that the magnetic bar could not stir again and the heating was continued at the same temperature until the considerable dryness was achieved. The product contain moisture due to incomplete dryness. It was also observed that, the more number of days the product being kept in the universal bottle the more the increase in the moisture content. The result was convincing and achieving but the percentage value of zinc was at higher value when compared to the value of macro-elements (NPK). This problem had been resolved by lowering the mass of Zinc sulphate heptahydrate that was used as the source of microelement. The percentage yield was calculated as = 63%

The chemical reaction step of the second procedure

$$NH_4H_2PO_4 + ZnSO_4.7H_2O \longrightarrow NH_4ZnPO_4 + H_2SO_4 + 7H_2O$$

$$NH_4ZnPO_4 + KCl \longrightarrow ZnPO_4 + NH_4Cl$$

$$KZnPO_4 + CO(NH_2)_2 \xrightarrow[\textbf{(90°C)}]{\text{(1 mL KOH)}} [K(CO(NH_2)_2)_2\,Zn]PO_4$$

2.1.3 Reaction method three (3) (with KOH)

The main objective for carrying out this reaction step is to further reduce the acidity of the product. The reaction method (1) was still maintained but after 20 minutes of heating, 2ml of KOH was added and the heating was between 90^{0}C – 110^{0}C. When ammonia gas began to evolve, the heating was still continued for another 2-4 minutes and the product was removed immediately and continuous scrapping from beaker with the aid of spatula was ensured before complete dryness when the product would have been completely hardened to the beaker. The scrapped product was a very dried, fine, white and free flowing crystal. The product was weighed and the mass was 18.25 g and the acidity reduced. The percentage yield was calculated as: =72%

The chemical reaction step of the third procedure.

$$NH_4H_2PO_4 + ZnSO_4.7HO \longrightarrow NH_4ZnPO_4 + H_2SO_4 + 7H_2O$$

$$NH_4ZnPO_4 + KCl \longrightarrow KZnPO_4 + NH_4Cl$$

$$KZnPO_4 + CO(NH_2)_2 \xrightarrow[\text{(90°C-110°C)}]{\text{2 mL KOH}} [K(CO(NH_2)_2)_2Zn]PO_4$$

2.1.4 Reaction method four (4) (with KOH and P_2O_5)

This reaction was aimed at increasing the phosphorus level of the product. The reaction was carried out according to method one above but after 15 minutes of heating 1ml of KOH was added followed by 1 mL of P_2O_5 after another 3 minutes. The heating was still at 90^{0}C – 120^{0}C and a white sticky product was obtained. The product was analyzed with atomic absorption spectroscopy and result of the analysis shows that, the ratio of the microelement and the macro-elements product which is Zinc-N-P-K complex fertilizer is **1:1:1:1.** . The percentage yield was 82%

The chemical reaction step of the fourth procedure.

$$NH_4H_2PO_4 + ZnSO_4.7H_2O \longrightarrow NH_4ZnPO_4 + H_2SO_4 + 7H_2O$$

$$NH_4ZnPO_4 + KCl \longrightarrow KZnPO_4 + NH_4Cl$$

$$KZnPO_4 + CO\,(NH_2)_2 \xrightarrow[\text{(90°C-120°C)}]{\text{1 mL KOH,1 mL } P_2\,O_5} [K(CO(NH_2)_2)_2\,Zn]PO_4$$

2.2 Metal analysis on AAS

The metals were analyzed using Model 210 VGP of the Buck Scientific AAS series with air-acetylene gas mixture as oxidant (Jones *et al.*, 1996). Extracts from the above digestion were aspirated and the equipment calibrated for each element. The results were recorded as mg L^{-1} of solution and were calculated to mg kg^{-1} of sample using the weight of sample taken as a denominator of the digest volume (50 ml). Calculation mg kg^{-1} sample = digest conc. X DF digest conc = Analyte reading on AAS

$$\mathrm{DF} = \frac{Vol\ of\ digest\ X\ aliquot}{wt\ of\ sample}$$

vol of digest = Final volume of digested or extracted sample aliquot = ratio of sample to distilled water (when diluted further) weight of sample = wt of sample taken for digestion or extract.

2.3 Electrical conductance of complexes

0.05 g of Zinc-N-P-K complex and each compound of ammonium dihydrogen phosphate, Zinc sulfate heptahydrate and urea was weighed and dissolved in 50 mL of distilled water. The electrical conductivity metre was put in the beaker that contain the dissolved complex and each of the dissolved compound. The electrical conductivity values with the unit in microsiemens were displayed on the electrical conductivity metre and each value was recorded accordingly.

3.0 Results and Discussion

Micro analytical measurement

Tables 1 represents elemental composition of Zn-based NPK fertilizer result found to be in 1:1:1:1 ratio.

The nitrogen (N), Potassium (K), Phosphorus (P) are in the same ratio (1:1:1:1) together with the value of Zinc. This result implies that, the fertilizer is very useful for the soil that is deficient of nitrogen, phosphorus, potassium and Zinc. According to the standard values and ratios of the various components of NPK fertilizer there can be 15-15-15(1:1:1), 20-20-20(1:1:1) 15-30-15(1:2:1).

Table 2, shows the results between the electrical conductivity and mobility of ions in the metal based fertilizer and their parent ligands, which revealed that Zn-NPK has higher concentration or population of ions.

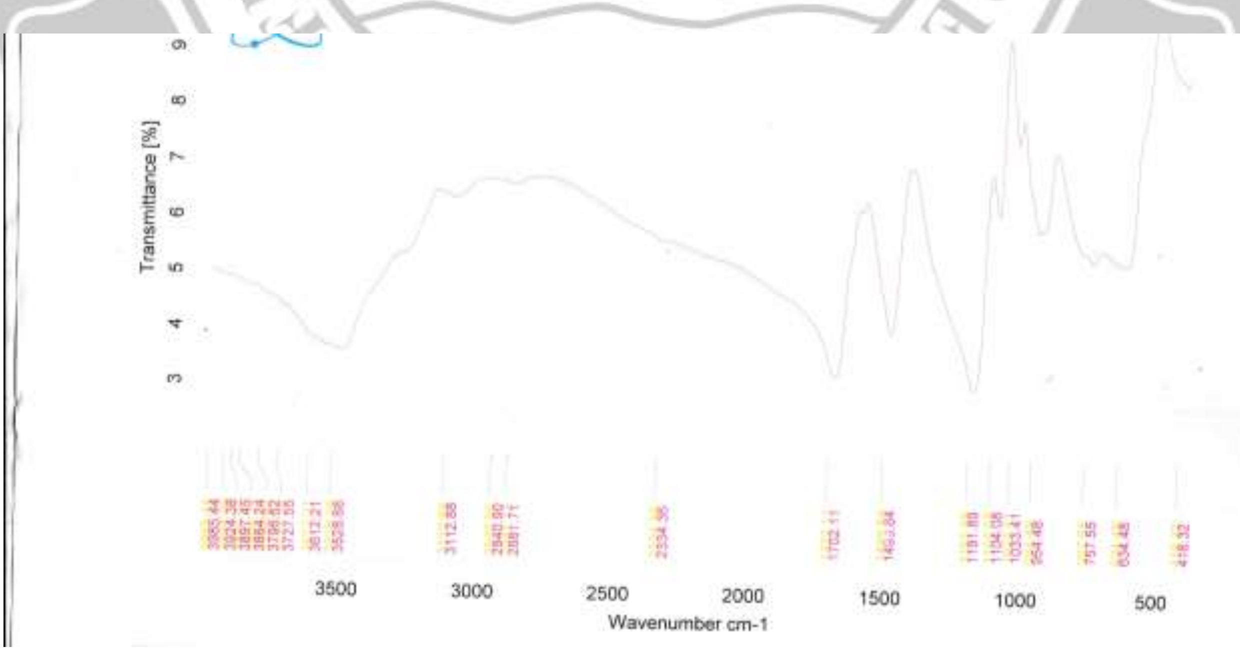

Fig 1: FT-IR of Urea

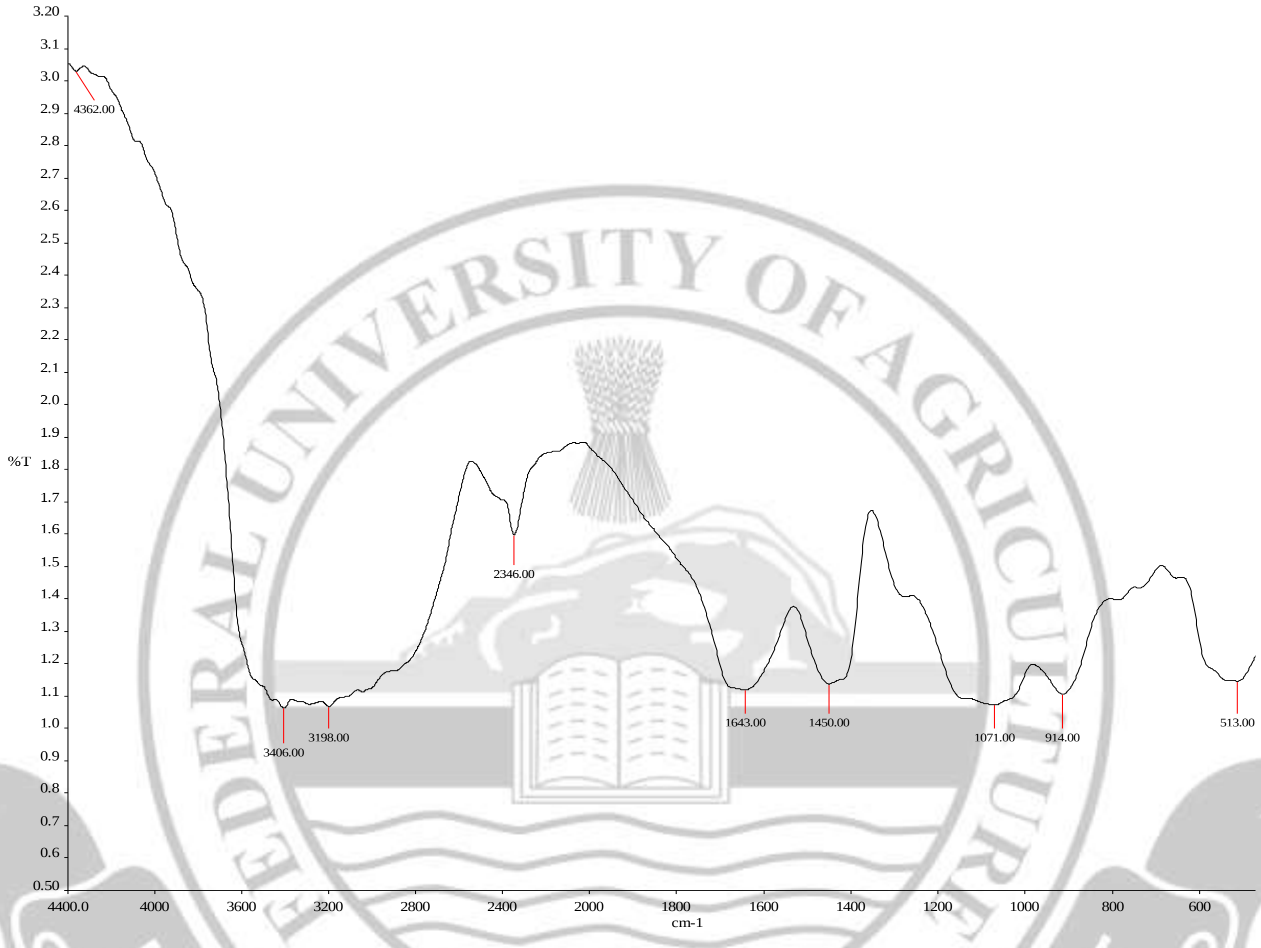

Fig 2: FTIR of Zn-NPK fertilizer

Table 1: Elemental composition in Zn-NPK Fertilizer

S/CODE	N%	P%	K%	Zn%
NPKZn	7.41	6.91	6.97	7.31
Ratio	1	1	1	1

Table 2: Electrical conductivities of Zn-NPK Fertilizer and micronutrients

Compound	Values (µS)
Zn-N-P-K	1471
$NH_4H_2PO_4$	878
$ZnSO_4.7H_2O$	651
$CO(NH_2)$	13

Infrared spectroscopy

In addition, the FT-IR spectra has shown in Fig 1. for the free fertilizer shows the presence of the major functional groups of the amine and carbonyls at 3500 cm^{-1} and 1702 cm^{-1} respectively from the urea while a bathochromic shifts to 3406 cm^{-1} and 1643 cm^{-1} due the zinc ions coordination around the free urea ligand. Absorption band at 634.48 cm^{-1} is attributed to Zn-C bond, this is revealed in Fig 2.

Conclusion

The synthesis and characterization of Zn-N-P-K fertilizer is very germane and well characterized. It is also needful to show that the synthesized products are good for application on land that is deficient of NPK and Zinc nutrients purposely for agricultural purposes.

References

Benton J.; Jr. "Inorganic Chemical Fertilisers and Their Properties" in *Plant Nutrition and Soil Fertility Manual*, Second Edition. CRC Press, 2012. ISBN 978-1-4398-1609-7. eBook ISBN 978-1-4398-1610-3.

Bodelier, L. E., Peter, R., Thilo, H., & Peter , F. (2017). Stimulation by ammonium based fertilizers of methane oxidation in soil rice roots. *International Fertilizer Association*.

Chien, S. H., Prochnow, L. I., & Cantarella, H. (2015). *Recent Developments of Fertilizer Production and Use to Improve Nutrient Efficiency and Minimize Environmental Impacts.*

Dobermann, A. (2005). Nitrogen use efficiency - State of the art. *Proceedings of the International workshop on Enhanced-Efficiency fertilizers.* Frankfurt, Germany: International Fertilizer Industrial Association.

Rai, M., Ribeiro, C., Mattoso, L., Duran, N., (2015) Nanotechnologies in Food and Agriculture. 1st edition, *Springer*.

European Fertilizer Manufacturers' Association. (2000). Production of NPK Fertilizers . In *Best Available Techniques for pollution prevention and Control in the European Fertilizer Industry* (p. 8). Belgium.

Garret,, H. (2014). *Organic Lawn Care: Growing Grass the Natural Way. .* Texa

Jones, J.B. H.A. M. Jr. (1996). Plant Analysis Handbook II: A practical Sampling, Preparation, Analysis, and Interpretation Guide. ISBN 1-878148-05-2.

Lide, D. R. (n.d.). Magnetic Susceptibility of the elements and inorganic compounds. Handbook of Chemistry and physics.

Motalvo, D. (2016, December 12). *International Zinc Association*. Retrieved March 28, 2019, from www.zinc.org: http:// www.zinc.org/sustainability-learning-annex/

Shriver, & Atkins' . (2017). *Inorganic Chemistry.* Oxford University Press. 2010. ISBN 978-0-19-923617-6.