PREPARATION AND ANALYSIS OF VARYING MOLAR RATIOS OF UREA-FORMALDEHYDE MODIFIED WITH RICE STRAW AS SLOW-RELEASE FERTILIZER.

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Abstract: Slow-release fertilizer (SRFs) are those fertilizer that releases plants nutrients over a given period at a rate that allows for maximum plant uptake, optimum plant growth and minimum fertilizer waste. This study aims to formulate and analyze varying molar ratios of urea-formaldehyde (UF) modified with rice straw as a slow-release fertilizer. Three different slow-release fertilizers were produced by combining a unit (1 mole) of urea to various molar ratios of formaldehyde; 2, 2.5 and 3 moles, to form 1:2, 1:2.5, and 1:3 UF respectively. Each of these fertilizers was modified with rice straw to be used as slow-release fertilizers. Fourier transforms infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) were employed to analyze the prepared fertilizers. This is to find out what makes them better fertilizers than the conventional urea fertilizers in use by farmers. The FTIR shows that the UF-modified rice straw has functional groups: --NH, -NH_2, -OH, C=O, and CH_2OH which must have interacted by condensation and hydrogen bonding. The SEM indicates that as the formaldehyde ratio in UF-modified rice straw increases greater number of small bright areas appear on the sample micrographs with clear indications of large micropores and surface areas for absorption. The functional groups – NH and – NH_2 are the nitrogenous nutrients from the UF which are slowly released to plants. The pores absorb water, which dissolves the nutrients and also provides the regulation of the supply of nutrients to plants. The amorphous nature of the samples from the XRD makes the process of the nutrients getting to the plants unhindered. The fertilizer formulation is recommended to fertilizer industries for production on a large scale to replace the present urea fertilizer in the market.

Keywords: Analysis, Modification, Rice-straw, Slow-release fertilizer and Urea-Formaldehyde

INTRODUCTION

There is a growing demand in the agricultural sectors of many countries to increase food production which leads to high demand for urea fertilizer. This is due to exponential growth in population, consequently environmental pollution, and hazardous gaseous emissions apart from its losses through volatilization and leaching. (Fayaz, *et al.*, 2019) The use efficiency of nitrogenous fertilizer by crops is about 50 % (Fayaz, *et al.*, 2019) Implying 50 % economic losses on the cost of the fertilizer which is transferred to the consumer.

Slow-release fertilizer (SRFs) are those fertilizer that releases plants nutrients over a given period at a rate that allows for maximum plant uptake, optimum plant growth and minimum fertilizer waste (Wang *et al.*, 2020). These advantages help in reducing environmental threats and promoting high crop yield. Straw return has been used to fertilize rice farms, which is a sustainable agricultural management practice that enriches the soil. It encourages nutrient balance, and supply of organic matter and micronutrients (iron, copper, molybdenum, manganese, boron and zinc) to the soil hence improving soil fertility (Huang, 2013). In a comparative study with other types of fertilizers, straw return gave a 5.4 % increase in rice yield, the highest being organic fertilizer with 7.8 % (Panel, 2018). The combination of urea formaldehyde and rice straw should give a better-performance fertilizer. In the present work, one mole of urea will be reacted with two moles of formaldehyde to give UF 1:2, one mole of urea with two and a half moles of formaldehyde to give UF 1:2.5. In the last

preparation, one mole of urea will be reacted with three moles of formaldehyde to form UF 1:3, the reaction for the formation is shown in the text; alkaline condensation reaction of urea and formaldehyde to form Mono-, di- and tri methylolureas. Each of the formulations will then be modified with rice straw and characterized.

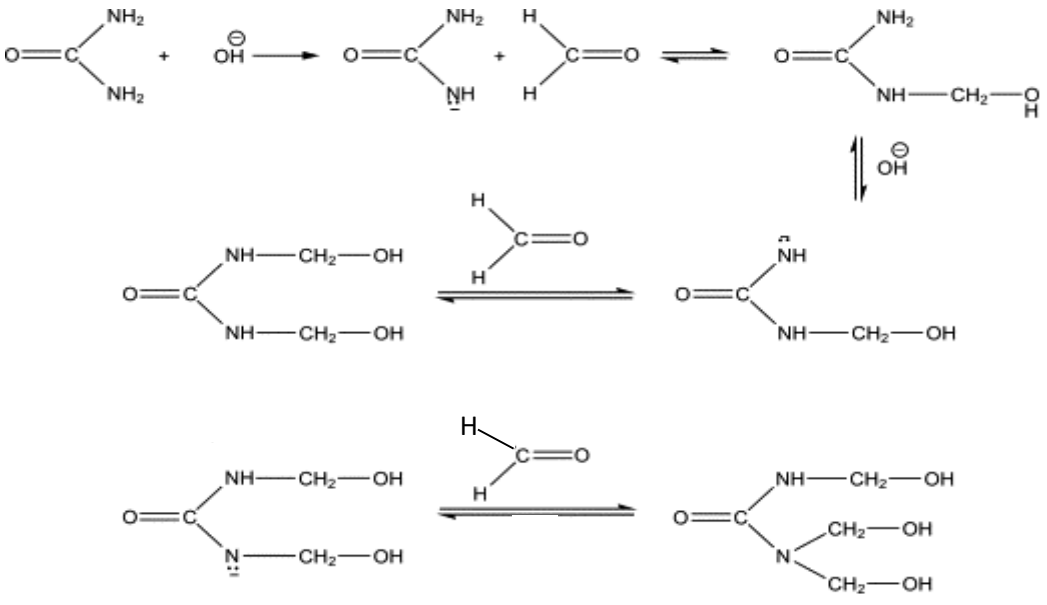
The use of conventional nitrogenous fertilizer has a 50% loss on application to the soil as a result of volatilization, leaching, denitrification and water run-off which is a huge economic waste. Water run-off with dissolved nitrogenous fertilizer results in environmental problems; Surface and underground water pollution. Hence the present study aims to formulate and analyze varying molar ratios of urea-formaldehyde (UF) modified with rice straw as a slow-release fertilizer.

MATERIALS AND METHODS

The urea used is a product of Kermel with a molecular weight of 60.06 g, while the formaldehyde is a product of Qualikem 37 to 41 g per volume. The rice straw was obtained from a rice farm at Samaru Kataf, Kaduna State. It was processed to a particle size of <0.5 mm.

Preparation of Varying Molar Ratios of Urea Formaldehyde Modified Rice Straw

198.6 ml (2 moles) of formaldehyde was measured into a beaker 60.06 g (1 mole) of urea was dissolved in the formaldehyde with the aid of stirring. The pH of the solution was adjusted to between 7 and 8 with drops of ammonia solution. The solution was poured into a Buchner flask and heated at a temperature of 40-60 ^{0}C for twelve hours with continuous stirring using a magnetic stirrer. The same process was done for molar ratios. 1:2.5(60.06 g of Urea with 248.3 ml of formaldehyde) and 1:3(60.06 g of urea with 297.9 ml of formaldehyde). The equation for the reaction is shown below.



Alkaline condensation reaction of urea with formaldehyde to form Mono-, di- and tri methylolureas.

Modification with Rice Straw

At the end of the twelve hours of heating the urea-formaldehyde formed was poured into a beaker where it was again heated to 100 ^{0}c for 30 minutes with stirring. 15 g of rice straw was added as stirring continued for 20 minutes. The resultant

pastry matrix was evenly spread on a tray and its content was heated in an oven at 70 ^{0}C for six hours for complete drying. The same procedure was done for each of the molar ratio combinations of urea formaldehyde (Nwufo, 2007).

Fourier transform infrared (FTIR)Spectroscopy

Fourier transform infrared (FTIR) spectroscope transmittance spectra were obtained with a spectrum 1000 Oxford Perkin-Eliner spectrometer in spectral area of 500-4000 cm^{-1} with a resolution of 3 cm^{-1} and 32 scans and was followed with a well outline procedure of analysis and serve as a direct means of for the identification of the surface functional groups Figure.1.

Scanning Electron Microscope (SEM)

The SEM micrograph of the prepared UF was examined in a SEM system (SEM) (JEOL) SM 840A- Oxford ISIS300. The samples were carbon coated to provide good conductivity of the electron beam; the operating condition of the instrument was in good form. The surface morphology of the UF-modified rice straws was studied. All the pictures were taken with 5000 x magnification. Characteristic micrographs of the samples UF modified rice straw ratios 1:2, 1:2.5, 2.3 and rice straw represented as samples B, C and D respectively, presented in plates 1-3 with Varying magnifications.

X-ray diffraction (XRD)

XRD analysis was performed on the solid UF adsorbents using Rigaku mini flex 600, 600 w x-ray tube with direction of Angle 2Ɵ and scanning range 3 ^{0} to 70 ^{0}. The Analysis report obtained is shown in Figure. 2-5.

RESULTS AND DISCUSSION

Mono-, di- and trimethylolureas are the products of the alkaline condensation reaction of urea with aqueous solution of formaldehyde. The formed UF-modified rice straw has surface functional groups of C=O, -NH and – OH which can react with macromolecular end groups mainly hydroxyl groups via condensation reactions (Mayo, 2012). During the first step of the addition reaction between urea and formaldehyde, (Babar, 2014) dimethylolureais produced have two hydroxyl groups and could interact with carbon and nitrogen compounds found within the rice straw matrixes to verify this during the formulation of UF rice straw hybrids, all samples were studied with FTIR spectroscopy and recorded spectra in Figure1

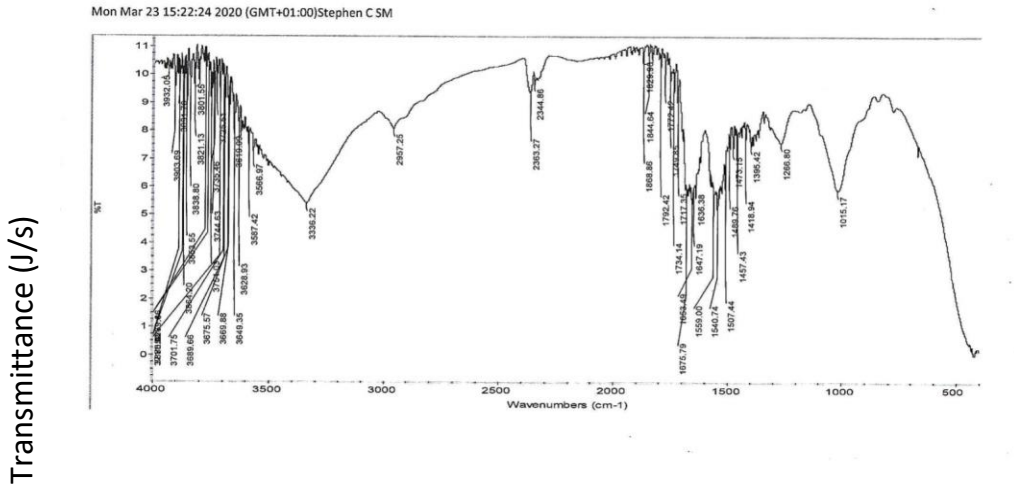


Figure. 1 FTIR Spectra of Urea Formaldehyde

The multiple and broad peaks on the UF (Figure.1) resins spectra broad peaks around 3885 cm^{-1} and 3841 cm^{-1} can be attributed to hydrogen –OH and –NH stretching vibrations of hydroxyl groups and primary and secondary amines. The fact that the bands are rather broad may be attributed to monomers such as water and formaldehyde whose –OH groups may form hydrogen bonds with reactive functional groups (Raymond, 2015) as CH_2OH, $-NH_2$ and –NH. Free $–NH_2$ groups have characteristic peaks of 3440 cm^{-1}. In the spectra of pure UF resin, the peaks are centred at the area of 3340 cm^{-1}, indicative that the amount of bounded–NH is higher compared to the free-NH_2 (Simer, 2003). The low-frequency values for the bands suggest that the hydroxyl groups may be involved in hydrogen bonding. The position of the band due to non-bonded –OH groups is usually above 3500 cm^{-1}. At 1541^{-1} cm is the stretching motion due to C=O.

SEM micrographs show large surface areas and as the formaldehyde ratio increases in UF (1:2, 1:2.5, 1:3), a greater number of small bright areas appear indicating large micropores and surface areas for absorption (Que, 2007) the analysis also revealed that bright spots seen are nanoparticles originated from ratio concentration in the UF modified rice straw. The surface area and bright spots become larger and more apparent as the formaldehyde ratio increases. The average size of the aggregates formed by the UF-modified rice straw particles in plates 3-5 at higher magnification is almost 150 nm, while the smaller and larger particles were also presented ranging between 50 and 350 nm.

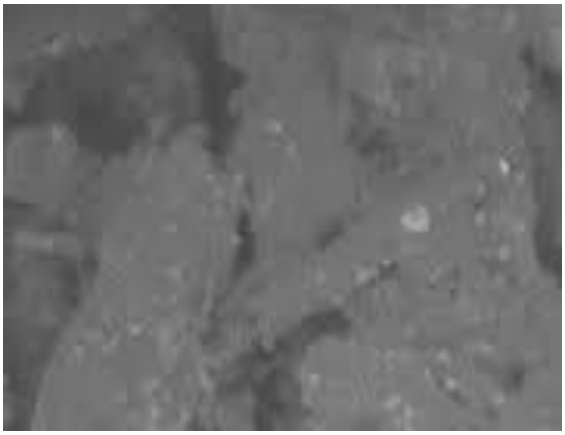


Plate 1, UF 1:2 showing micro pores

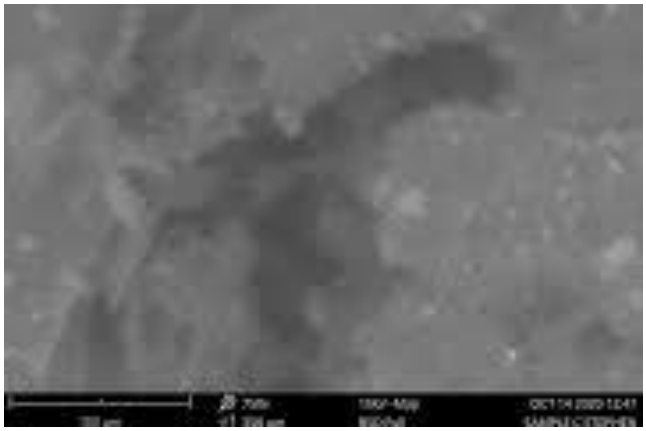


Plate 2, UF 1:2.5 showing microspores

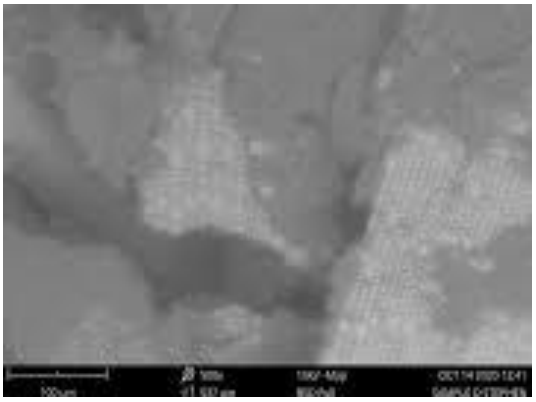


Plate 3, UF 1:3 showing micro pores

The XRD pattern of pure rice straw (F) consists of a broad different peak at 23^{0} which is proof that it is an amorphous material. The varying ratios of the UF-modified rice straw present

relatively sharp peaks at UF, B (21^0) along with peaks at UF, C (22^0) and UF, D (22^0) as reported (Zarba, 2008). The XRD pattern of samples also confirms that all the preparations are mainly amorphous with a small degree of order.

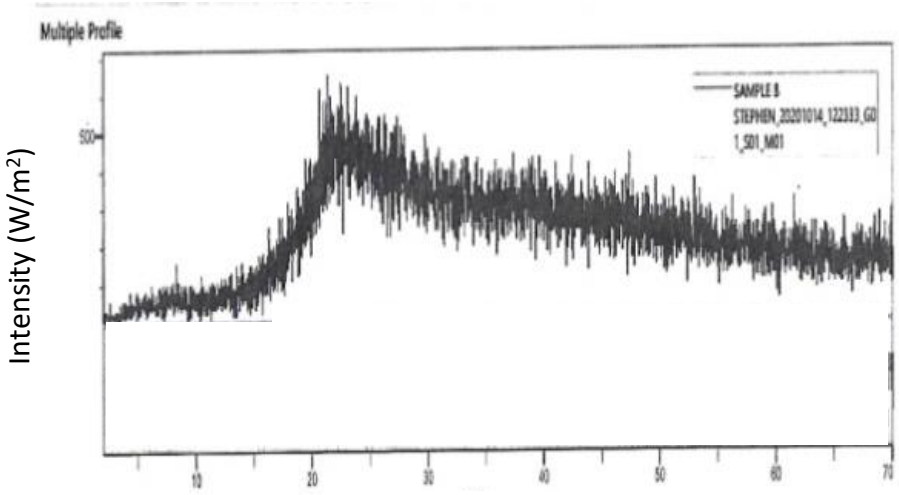


Figure. 2: XRD pattern of UF 1:2(B)

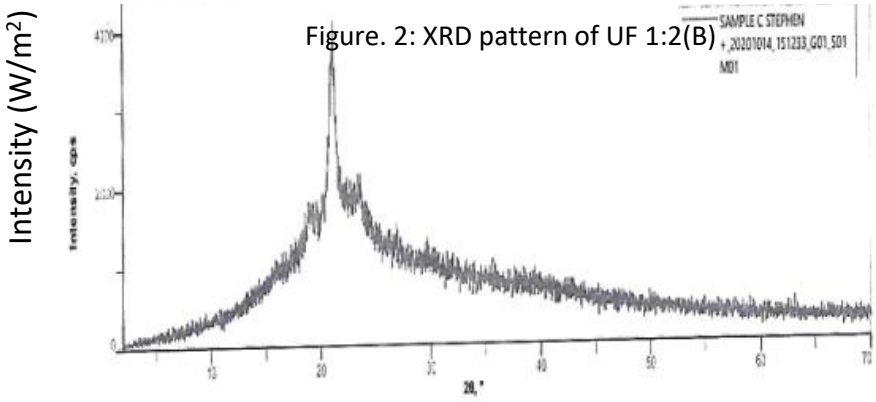
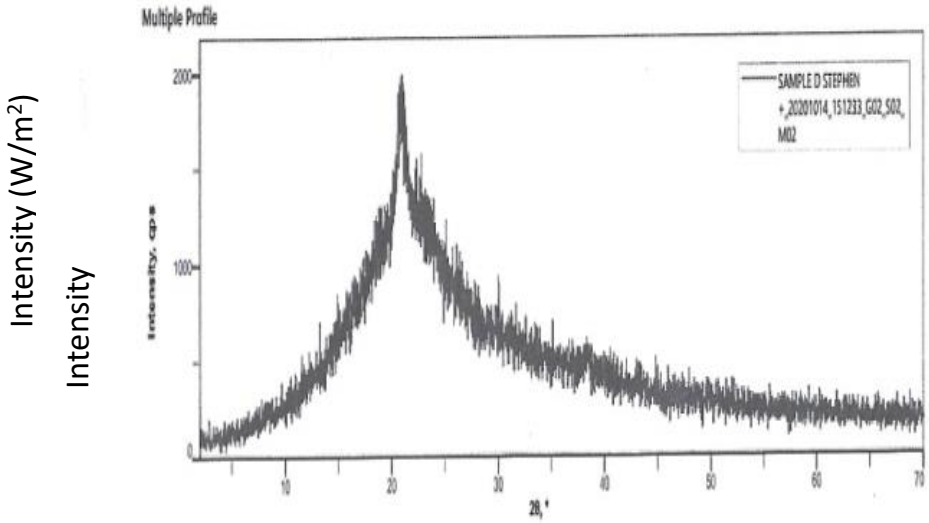


Figure. 3: XRD pattern of UF 1:2.5(C)



2(theta)
Figure 4: XRD pattern of UF 1:3(D)

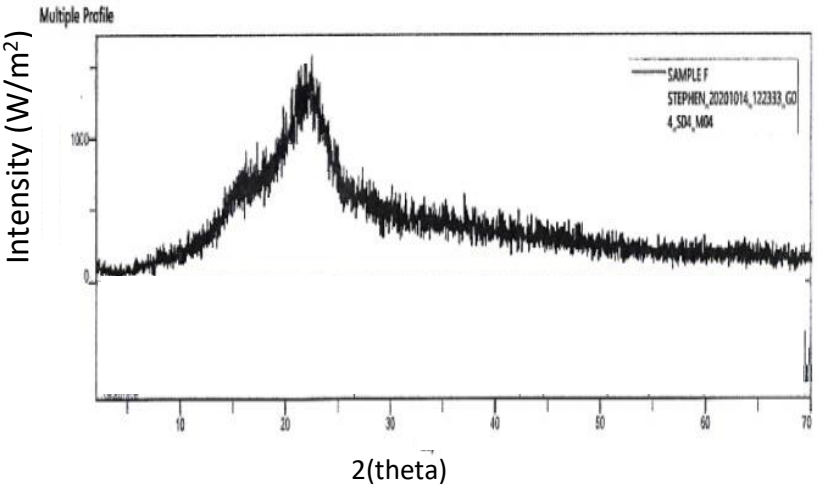


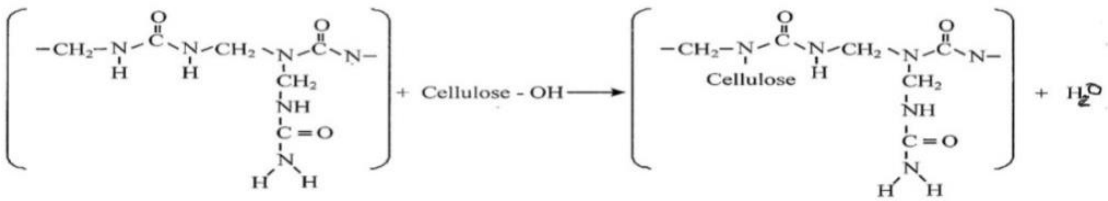
Figure. 5: XRD pattern of rice Straw

CONCLUSION

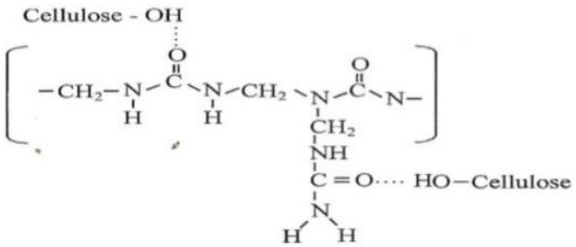
The condensation reaction between urea and formaldehyde in the preparation and modification of the varying molar ratios of Urea formaldehyde helps it to release nutrients slowly. The functional groups $–NH_2$ –NH provide the nitrogenous nutrient. The pores in the matrix increase in size and number as the UF molar ratio increases, it regulates the nutrient release by absorption of water which dissolves the nutrient. This adds to the slow-release character. The amorphous nature makes the process of the release to the plants unhindered. The rice straw added improves soil quality. Unlike conventional urea which has about 50% economic losses and environmental problems due to volatilization, leaching and dissolved urea in water run-off.

Equations showing possible ways rice straw is attached to UF.

1. Covalent bond by condensation



2. Hydrogen bond formation



Recommendations

The fertilizer formulations are recommended to fertilizer industries for production on a large scale to replace the present urea fertilizer in the market. More work will need to be done by researchers on the determination of cold and hot water insoluble nitrogen. Field trials will also have to be performed to bring out additional qualities that are of advantage over the urea fertilizer in the market.

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