IMPACT OF IMMOBILISED ALIPHATIC AMINES USING SOFT AND HARD LIGNOCELLULOSIC MATERIALS FOR INHIBITING *STRIGA HERMONTHICA* INFESTATION IN MAIZE (*ZEA MAYS*) FIELD

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ABSTRACT
Parasitism of weeds have increased dependence on inorganic fertilizers, herbicides and chemicals to maintain adequate weeds control which are detrimental to crop nutrient quality, taste, soil fertility, retention of nutrients, water and the environment through nitrate leaching and eutrophication. This work examined the impact of nitrogen fertilization of Methylamine and Trimethylamine to maintain high nitrogen humus that increases the performance of cereal crops under striga infestation with soft and hard lignocellulosic materials as soil conditioners. The physiochemical parameters showed characteristic functions for Chemical modifications. The unmodified and modified sawdust were run under FT-IR to know the extent of modifications. The result revealed that the sawdust were oxidised at 0.02-1.0M KIO_4 but limited on 0.02-0.04M KIO_4. The immobilised soft sawdust of 0.05-1.0M Methylamine, 1.0M Trimethylamine and the immobilized hard sawdust of 0.05-1.5M methylamine on the sprouting maize showed progressive growth but lower compared to 0.05-1.5M Trimethylamine that inflamed part of the crop. Soft wood showed better fertilization than hard wood and 0.05-1.5M of the amines suppressed S. hermonthica from gradual to complete absence. Understanding these fertilization strategies, which enhance the competitive ability of crops while reducing interference from weeds will benefit small-scale farmers, agrochemical industries and control environmental pollution.

Keywords: *Aliphatic amines, chemical modification, inhibiton, lignocellulosic material, maize, Striga hermonthica.*

1.0 INTRODUCTION
Lignocellulosic material is one of the most abundant renewable resources and natural polymer material (Yang et al., 2011) that have the potential to nitrify soil to support large-scale food production among other fields of fuels, chemicals, polymers. Such low value residue includes a variety of materials as sawdust, sugarcane bagasse, rice husk, wheat bran, maize cob, among others (Eriksson et al., 1993). Cellulose, hemicellulose, and aromatic polymer lignin comprise the main composition of cell walls of plants and are important components of natural lignocellulosic materials (Shambe et al., 1993; Yu et al., 2010; Rowell, 2012; Lee et al., 2014). Cellulose is an unbranched homopolysaccharide consisting of D-glucopyranosyl units, which are linked together by β-(1→ 4)-glucosidic bonds. Hemicelluloses are branched heteropolysaccharides designate the conformation of the hydroxyl group at carbon 4 (C-4) for pentoses (xylose and arabinose) and C-5 for hexoses (glucose, galactose, and mannose) sugar residues, which may also carry

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ISSN: 2016-1303 | Web: www.cjpas.fulokoja.edu.ng

acetyl groups. Lignin consists of phenylpropane units linked together by different types of inter unit linkages in which the ether bonds are the most common (Shambe, et al.,1993; Rowell, 2012).

Oxidation of these bio-polymeric hydroxyl groups involves functional group transformations using reagents. For this work, periodate is essential, an anion composed of iodine and oxygen, it is one of the oxy-anions of iodine which is the highest in the series of perhalogenates (Hill,1998). Periodate cleavage is often utilized in molecular biochemistry for purposes of modifying saccharine rings, as many five- and six-membered ring sugars have vicinal diols. This reaction has been used to determine the structure of monosaccharide (Feikema, 1996; Telvekar et al., 2013).

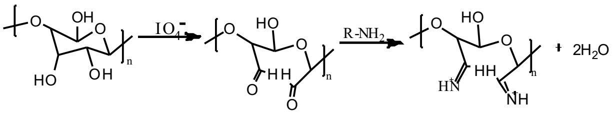

Figure 1: Periodate cleavage of a vicinal diol to monosaccharide to Schiff base (imine)

Sawdust, a soil conditioner, immobilized to gain nitrogen base sawdust is particularly useful when incorporated with heavy soils to balance the excess carbonaceous matter and meet the requirements of microorganisms that slowly decompose the woody material (Chen et al., 2014).

Joseph and James, (1963) investigated Periodate modification of polygalactose-mannose gum which shows that galactose is preferentially attached to periodate and partially substituted with aldehydic function due to the formation of carbonyl group during the cleavage, which change the molecular structure of the gum. In like manner, Sridhar et al., (2001); Rinaudo, (2010) gave an encouraging reports of the treatment of sawdust by periodate oxidation which allows the introduction of two aldehydic groups that enhance the flexibility of cellulosic backbone and decrease molecular weight as intermediate for preparing cellulosic derivatives. These manifestations echo what Chen et al., (2014), reported for composite fabrication. Ibrahim et al., (2007) were able to synthesize and characterized some Schiff base by condensation of variety of aromatic amines. Rindap et al., (2017) in their earlier work had reported that sawdust could be utilized for humus maintenance using Dimethylamine and Aniline, which in this case Methylamine and Trimethylamine need to be explore as stated in this work. In recent years, there has been more stress on two aspects of societal importance: utilization of renewable resources to increase their utilization without allowing them go waste and the environmental safety whereby any product including waste should be biodegradable without adding to environmental pollution (Trombetta et al. 2010). Maize (*Zea mays*) is a cereal crop which is not native to Africa but through various introductions, has expanded from lowlands to highlands as well as from the marginal to optimal soil fertility environments. Nigeria has responded to the alien nature in Africa and its resemblance to native sorghum (Rich and Ejeta, 2008) and was rated in 2010 as the largest producer in Sub-Sahara Africa yielded 7.7 million tons from the total world production of 844M tons depicting 0.9% of the world production (Olaniyan, 2015). America produced 40% of the world harvest among other top producing countries like China, Brazil, Mexico, Indonesia, India and Argentina (Osman et al., 2013). Maize production in Nigeria is still at low case due to biotic, abiotic agronomic stresses prevalent in the continent, including soil infertility, pests and diseases, drought, unavailability of improved germplasms, striga and many others (Rich and Ejeta, 2008; Olaniyan, 2015) which has made farming unattractive venture.

Farmers are devastated by the challenge of striga weed. This Menace have been recognized as the greatest biological constraint to food production in Africa (Osman et al., 2013; Teka, 2014; Sarmiso, 2016). Striga infects important cereal crops such as maize, sorghum, pearl millet, finger millet and upland rice, causing substantial losses in yields in sub-Saharan Africa, thereby limiting food supply in many developing countries (Joel 2000; Scholes and Press 2008). It affects the life of more than 100 million people in Africa and causes economic damage equivalent to approximately 1 billion $US per year (Labrada, 2008; Waruru, 2013). Farmers have reported losses between 20% and 80%, and are eventually forced to abandon highly infested fields (Atera and Itoh, 2011).

Striga hermonthica among others striga species that affect maize are *S. alectica, S. asiatica, S. aspera, S. passargei and S. forbessii* (Kim, 1988). They are holoparasite, which depends solely on host plant for the supply of water, nutrient and energy for its survival (Stump, 1994). Even though specific chemical signals produced by the host plants provides the chemical stimulant for the seed germination (Okonkwo, 1966b; Cechin and Press, 1993; Shambe et al., 1996; Kuiper, 1997; Pegeau et al., 1998; Rich and Ejeta, 2008). *Striga hermonthica,* the annual hemi-parasites weed of monocotyledonous plant is among the most specialized root-parasitic plants (Emechebe et al., 2004; Dashak and Shambe 2005; Gurney et al., 2006; Kountche et al., 2013). *S. hermonthica* quickly adapt and can withstand a wide range of climate conditions (Sauerborn, 1994; Rich and Ejeta 2008), parasitized different host and is responsible for about 40% less of maize and millet in Africa thus compounding the food insecurity problem faced in African countries (Emechebe et al., 2004; Gurney et al., 2006).

This work therefore observed the physical properties, pretreatment and chemical modifications of the important natural components of the lignocellulosic material using Methylamine and Trimethylamine on maize field to know the effect on the crop and striga weed to address the heart beats of farmers for a sustainable maize production.

2.0 MATERIALS AND METHODS

2.1 Samples Collection and Treatments

The Sawdusts of *Tectona grandis* (soft wood) obtained from sawmills in Timber Market and woodwork workshops at Katako Market, Jos, Plateau State, Nigeria was screened to remove impurities while the Sandy soil sample was obtained within Shandam Local Government Area of Plateau State, Nigeria by mechanical method. The soil was collected at 5-10cm depth, was homogenized, air-dried and stored in sealed polythene bags for use in the laboratory. The sawdust samples sizes were distributed by impact sieve shaker (SV003) to obtain 2.00mm, 1.00mm and 0.50mm mesh sizes. Each sieve size particles was collected into a label plastics bags for analysis.

2.2 Determination of Physiochemical Parameters

The physiochemical parameters were analyzed using the following methods or procedures according to (AOAC, 1980). Each treatment of about 1g of sample in triplicate was expressed in percentage content; Moisture content was determined by oven dried method and Ash content was achieved by muffle furnace ashing method. Mean value of 1.0g of each mesh size was used for water absorptivity for different lengths of time (1 to 36 hours) as earlier specified by Rindap et al., (2017).The weight gained of samples after vacuum filtration was expressed as percentage water absorption capacity.

2.3 Oxidizing the Samples

Sawdust weighing about 1.0g were treated with various concentrations of potassium periodate (0.02 - 0.1 Moldm^{-3}) according to (Collinson and Thielemans, 2010; Rinaudo, 2010; Rindap et al., 2017).

2.4 Immobilization of Nitrogenous Bases on Oxidized Sawdusts

Methylamine and Trimethylamine was incorporated on the oxidized sawdust by weighing about 1.0g of the oxidized sawdust in 100ml of 0.5-1.5moldm^{-3} of each amine as described by (Datta et al., 2013; Mohamad et al, 2015)

2.5 pH of Soil Sample

Air dried soil sample of about 10g was prepared for pH reading according to (Wiberg, 2001)

2.6 Planting of Maize Seedlings and Immobilization on Soil

Perforated plastic buckets filled with the sandy soil sample to about two – third of the bucket, S. hermonthica seeds was spread, followed by maize seeds planting and immobilized saw-dusts were applied based on the concentrations and all labeled according to Rindap et al., (2017). The control was also observed.

2.7 Fourier Transform Infra-Red (FT-IR)

FT-IR spectra of un-oxidized, oxidized and immobilization sawdusts were measured with a Fourier transformed infrared spectrophotometer (FT-IR P8400S) to elucidate the functional groups present in the saw-dusts as outlined by (Silverstein et al., 1974; Morrison and Boyd 1997; Solomon and Fryhle, 2007).

3.0 RESULTS AND DISCUSSION

3.1 Physiochemical Parameters

Table 1: Percentage Mean Moisture and Ash Contents

Mesh Sizes	0.5mm	1.0mm	2.0mm
% Mean Moisture Content ±SEM			
Tectona grandis	3.90±0.20	4.20±0.20	4.60±0.10
Anogeisus leiocarpus	3.80±0.10	4.20±0.10	4.30±0.10
% mean Ash Content ±SEM			
Tectona grandis	2.67±0.06	2.65±0.06	2.64±0.02
Anogeisus leiocarpus	2.80±0.02	2.76±0.05	2.75±0.03

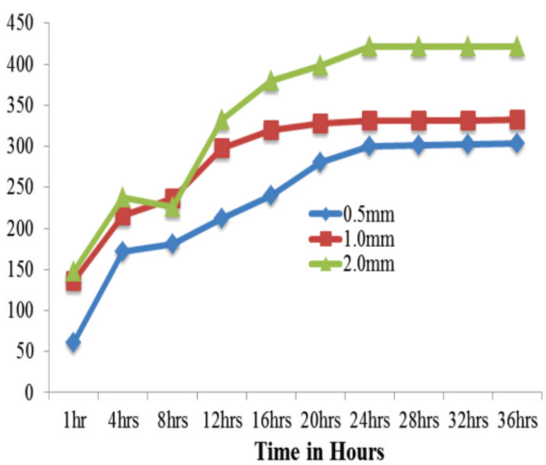

Figure 1: Water absorption capacity of *Tectona grandis* (softwood)

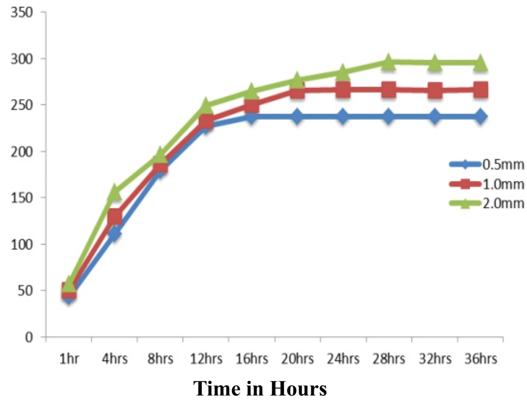

Figure 2: Water Absorption Capacity of *Anogeisus leiocarpus* (Hardwood)

The results obtained in Table 1 for *Tectona grandis* and *Anogeisus leiocarpus* lignocellulosic materials of 0.5-2.0mm particle sizes, deduced that the moisture content increases with increasing particle sizes with smaller particle sizes retaining more moisture for both materials as earlier maintained by Adhikary et al., (2008); Trombetta et al., (2010). It proposes to say that smaller particle sizes will expatiate the chemical modifications adapted by this work to investigate its effect on plant nutrients.

The water absorption capacity depicted in Figure 1 and 2 revealed increase with increasing particle sizes and time. This support the previous works of other authors Clemons, 2002; Adhikary et al., (2008); Trombetta et al., (2010) which concluded that it is associated with the surface area, hydrogen bonding of water, exposed hydroxyl group of cellulose, hemicelluloses and lignin of the supporting material. However, Rinaudo, (2010) attributed also that water solubility depend on the distribution of methyl substituent along the cellulosic backbone. The high moisture content and water absorption capacity of the saw dusts shows adequate support for absorption and retention of soluble nutrients that can easily be lost because of leaching, and with time can gradually release the nutrients for utilization by plants since the rate of decomposition of sawdust is very slow (Barbarick, 2014).

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ISSN: 2016-1303 | ***Web:*** *www.cjpas.fulokoja.edu.ng*

The ash content decrease with increase particle size of the sawdust as earlier reported by Demirbas, (2004) stating that a lignocellulosic materials with high ash is associated with fine particle size. Showing that the sawdust contains high organic components, which assist in retaining moisture as well as provide medium for nutrient utilization by plants (McNamee et al., 2015; Demirbas, 2004; David, 2014).

The pH value of the soil sample (4.90 ± 0.10) indicates that it is acidic. Many studies have shown that the solubility of elements in the soil is pH dependent and acidic soil favor iron solubility (Chuan et al., 1996; Skyllberg, 1999; Iqbal, 2012) but affect availability of Nitrogen and Potassium that are most needed nutrients for plants (Larsen et al., 2015). In addition, microbial activities can be destroy at low pH resulting in the accumulation of organic or plant remains thereby reducing the level of nitrogen obtainable from organic sources as stated in many earlier works (Zahran, 1999; Nakhro and Dkhar, 2010; Balota and Chavas 2010; Sharma et al., 2013). Furthermore, low pH can hydrolyze the tender roots of crops, which can result in the release of exudates. These exudates contained organic stimulants, which can stimulate the germination of Striga seeds as reported by Rich and Ejeta, (2008) such activities however, are slow down as a result of the immobilized nitrogenous bases on the lignocellulosic materials. There is counter activity that encourage release of the bases into the soil thus reducing the effect of the acidic exudates. In effect, there is reduced striga germination because of the basic environment in the soil.

3.2 Infrared Spectrophotometric Analysis

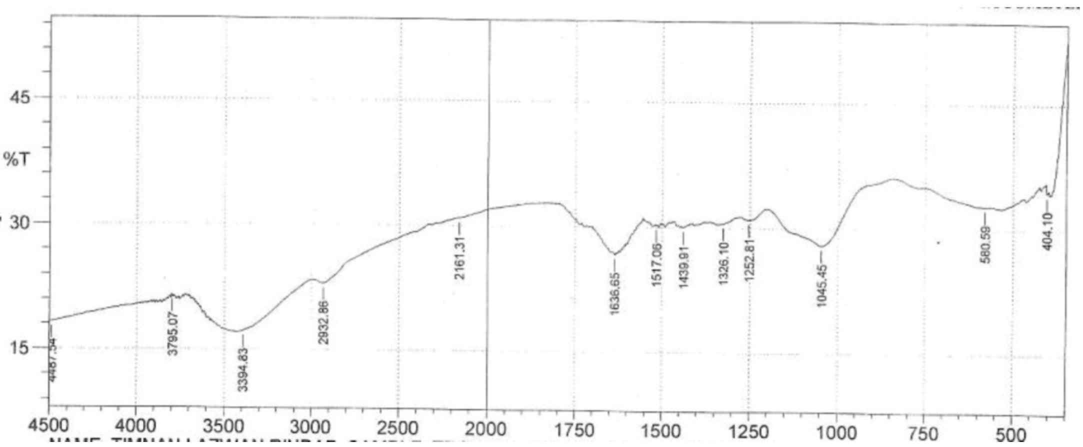

Fig. 3: IR spectrum of *Tectona grandis* (Un-oxidized)

Fig. 4: IR spectrum of *Tectona grandis* 0.02M KIO_4

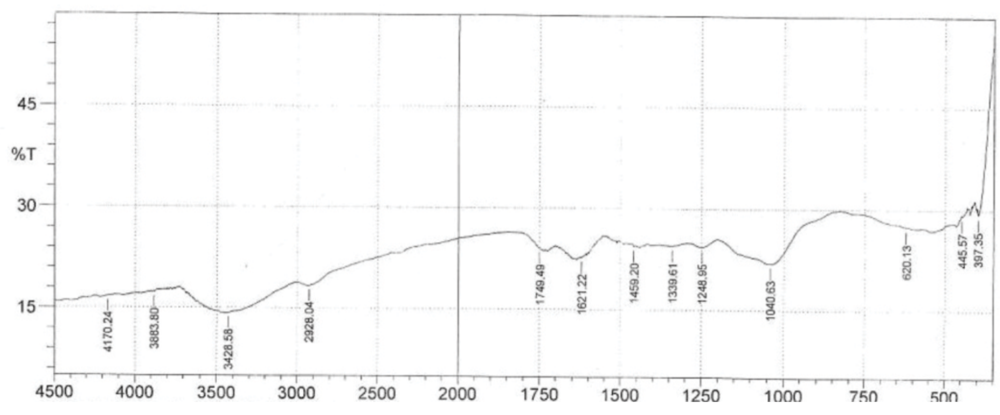

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Fig. 5: IR spectrum of *Tectona grandis* 0.1M KIO_4

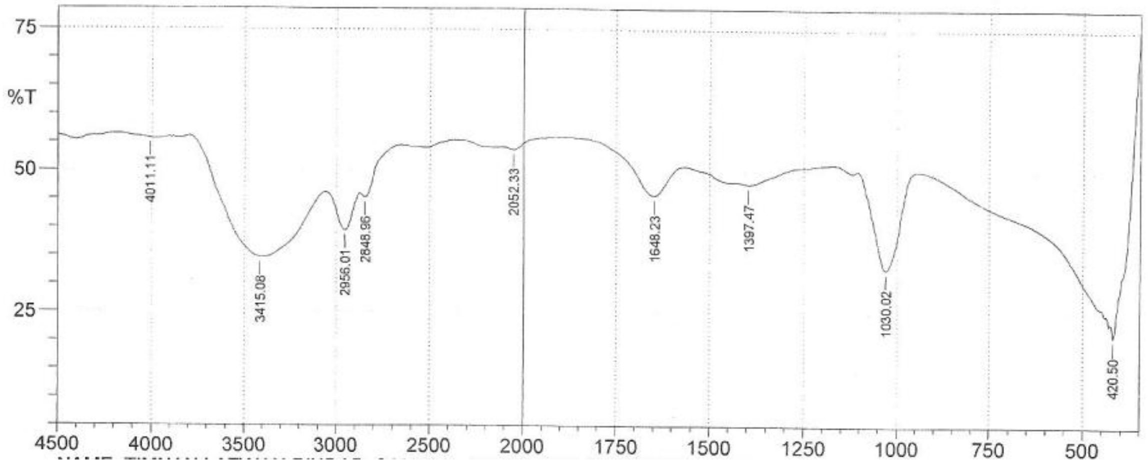

Fig. 6: IR Spectrum of *Anogeisus leiocarpus* 0.02M KIO_4

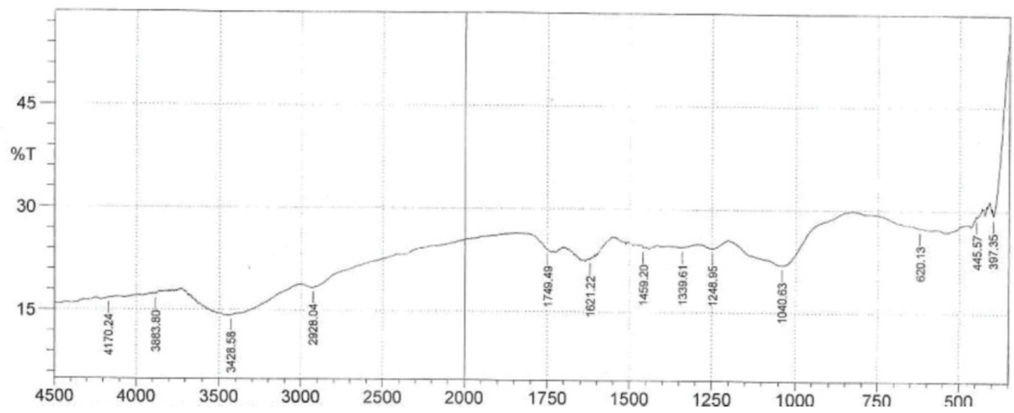

Fig. 7: Spectrum of *Anogeisus leiocarpus* 0.10M KIO_4

The infrared results are presented in Figure 3-11 for unoxidized, oxidized and immobilized sawdusts. The unmodified saw dusts exhibited broadband at 3475.84 and 3373.61cm^{-1}, which is due to O–H groups stretching. These bands are attributes of high concentration of phenols and alcohols. The intermolecular O–H stretching vibration band of unmodified sawdust spectrum in the range 3437cm^{-1} appeared broader compared to the oxidized saw dusts suggested to be as a result of water, hydroxyl groups from polyphenolic material contained in the unoxidised samples.

The absorption bands in the region 1749.49-1729cm^{-1} found in 0.02-0.04M KIO_4 oxidized saw dusts indicate the presence of carbonyl compounds, carboxylic acids and it derivatives. The dense band of O–H groups by glucose units of the cellulose polymer broadened the peak at 1550–1610cm^{-1} which was contributed by C=O bonds. The absorption bands at 2956.01 and 2880. 23cm^{-1} are due to the C–H stretching of the aldehydes group. Likewise the region between 1740-1685cm^{-1} shows C=O stretch for aldehydes and ketones. These regions evidenced the oxidation of the raw sawdust to a dialdehyde thereby stating that Oxidized sawdust of lower concentrations (0.02 and 0.04) did not show carbonyl absorption as also agreed by Dash, (2012).

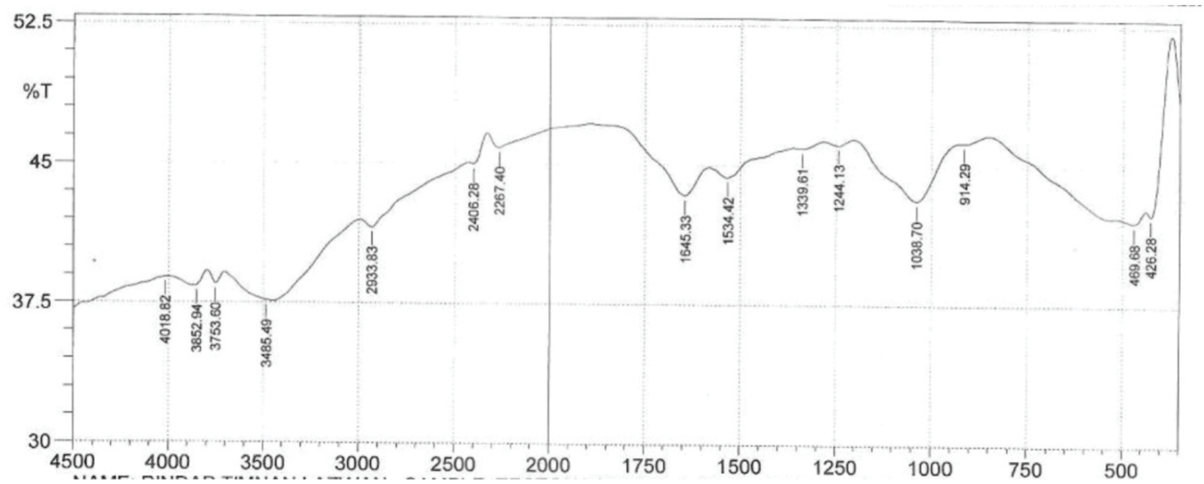

Fig. 8: IR spectrum of *Tectona grandis* 0.5M CH_3NH_2

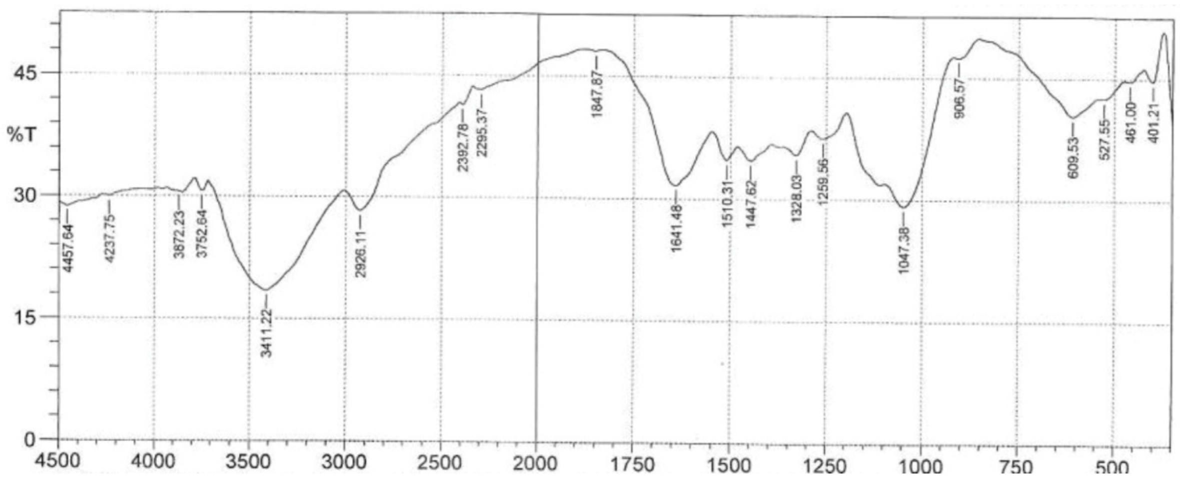

Fig. 9: IR spectrum of *Tectona grandis* 0.5M $(CH_3)_3N$

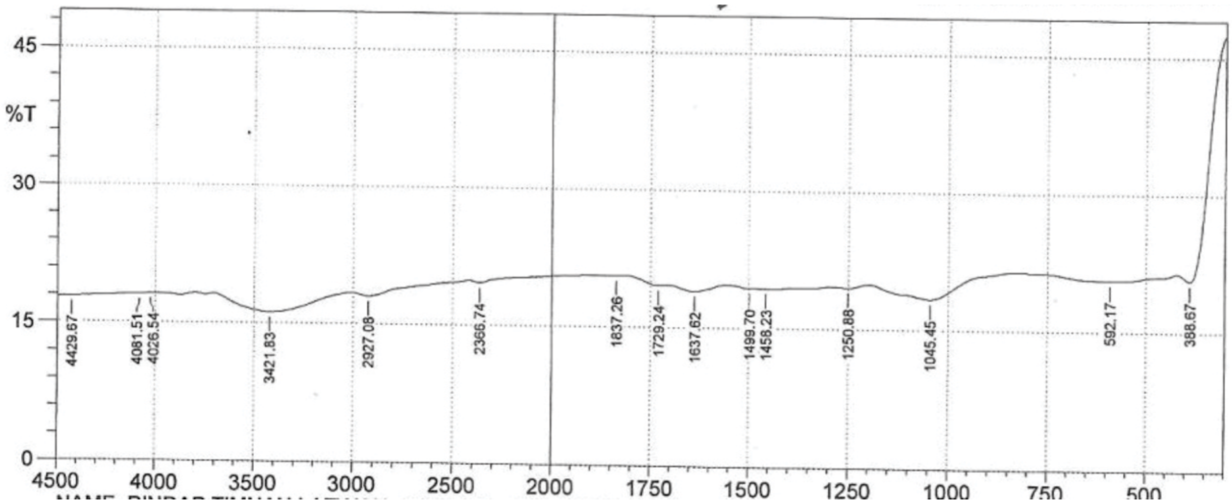

Fig. 10: IR spectrum of *Anogeisus* leiocarpus 1.0M CH_3NH_2

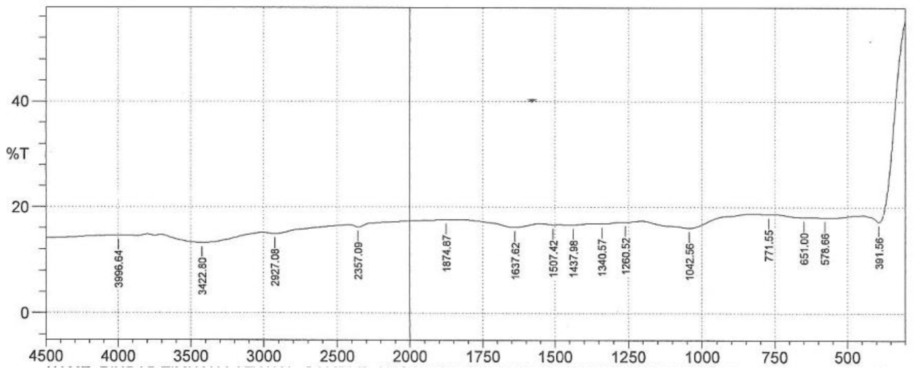

Fig. 11: IR spectrum of *Anogeisus leiocarpus* 1.0M $(CH_3)_3N$

IR spectra for the immobilized sawdusts depicted in Figures 5 and 6, shows that the N–H stretch for amines is between 3493.20-3402.54cm^{-1} which is due to hydrogen bonding between the amides. In addition, the N-H bend at the region 1650.15-1244.13cm^{-1} are for amines, amide and oximes. The C=O stretching of amides occurs at longer wavelength than normal due to resonance effect. The C-N stretch at 1640.15-1244.13cm^{-1} and C-H stretching at 2960cm-^{1} - 2860cm^{-1} are mainly for amides and oximes. All these absorptions showed that the amines were incorporated to the oxidized sawdust (Silverstein et al., 1974; Morrison and Boyd, 1997; Solomon and Fryhle, 2007).

3.3 Effect of Immobilized Sawdust on Maize and *S. hermonthica*

Incorporated methylamine and trimethylamine sawdusts base on concentrations were applied on sprouting maize plants with *S. hermonthica* aside control.

Germination of the maize seeds was within 3–5 days of planting. The maize sprout up healthy and after 2 weeks of germination, there was decreased growth, greenish to yellowish colorations of leaves which may be as a result of soil acidity, nutrients deficiency and competition with infested striga as also discussed by Watling and Press, (2001); Rank et al., (2004).

First application of modified (immobilized) Sawdust on sprouting maize was after 3 weeks and thereafter 2 weeks of germination on all the labeled samples. After the first application the soil environment was significantly modified to be basic therefore allowing the maize to germinate and grow without any detrimental effect of the striga weed. (Clemons, 2002; Adhikary et al., 2008; Acharjee et al., 2011)

Nevertheless, on second and third application (Plates 1-14), there was drastic improvement in maize growth but less pronounced growth of striga weeds meanly as a result of the strong root system of the maize that the striga cannot penetrate and live (Sarmisa, (2016); Rindap et al., (2017).

3.4 The effect of Concentrations of Methylamine (MA) Immobilized Soft Sawdust on Sprouting maize and *S. hermonthica*

P.1: Control

P. 2: 0.5mol/dm^3 MA

P. 3: 1.5mol/dm^3 MA

P. 4: 1.5mol/dm^3 MA

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3.5 The effect of Concentrations of Trimethylamine (TMA) Immobilized Soft Sawdust on Sprouting maize and *S. hermonthica*

P. 5: 0.5mol/dm^3 TMA

P.6: 1.0 mol/dm^3 TMA

P.7: 1.5 mol/dm^3 TMA

3.6 The effect of Concentrations of Methylamine (MA) Immobilized hard Sawdust on Sprouting maize and *S. hermonthica*

P.8: Contol

P 9: 0.5mol/dm^{3}MA

.10: 1.0mol/dm^3 MA

P 11: 0.5mol/dm^3 MA

3.7 The effect of Concentrations of Trimethylamine (TMA) Immobilized hard Sawdust on Sprouting maize and *S.hermonthica*

P 12: 0.5mol/dm^{3}TMA

P 13: 1.0mol/dm^3 TMA

P 14: 1.5mol/dm^{3}TMA

4.0 CONCLUSION

From this study it can be deduce that the use of modified sawdust on crops will help in controlling nutrient leaching and runoff water couple with it high water absorption and moisture content. Growing evidences have also shown that the solubility of most needed plant nutrients and microbial activities are hampered at high pH and low pH respectively thereby, this work have shown that there are potentials in the processes to correct and harness crop productivity. In addition, concentrations are factor to consider for effective use of immobilized nitrogenous bases sawdust on maize field and *Striga* weeds.

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