

Full Length Research

UTILIZING THE EFFECT OF IMMOBILISED ALIPHATIC AMINES AS ORGANIC FERTILIZER THROUGH SOFT LIGNOCELLULOSIC MATERIAL FOR CONTROLLING *STRIGA HERMONTHICA* IN MAIZE (*ZEA MAYS*) FIELD.

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ABSTRACT

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Striga control in crops need a variety of chemical modifications approaches that are based on increased knowledge of the weed intricate morphology that lead to its fascinating parasitism. Increased dependence on inorganic fertilizers, herbicides and continuous tillage to maintain adequate weed control has not solve the problems owing to the fact that these practices decreases soil fertility, retention of nutrients, water and has form complex chemical and physical changes in the soil. This work utilises methylamine and trimethylamine to maintain high nitrogen humus that increases the performance of cereal crops under striga infestation and lignocellulosic material of *Tectona grandis* as the soil conditioner. The moisture content and water absorption capacity shows characteristic functions for chemical modification as they increases with increasing particle size and time while ash content decrease with increase in size. The unoxidised, oxidised and immobilised sawdust were examined under FT-IR to know the extent of modifications. The result shows that all modification were effected to some extent were 0.02 and 0.04M KIO_4 were unable to oxidised the sawdust but was possible with higher concentrations of KIO_4 . The effect of immobilised bases were best at 0.05-1.0M methylamine and 1.0M trimethylamine on the sprouting maize while 0.05-1.5M of the amines shows gradual to complete absence of *S. hermonthica*. Understanding these basic mechanisms and timing of nutrient uptake in weeds and crops can lead to fertilization strategies, which will enhance the competitive ability of crops while reducing interference from weeds.

Keywords: Aliphatic amines; Chemical modification; Lignocellulosic material; *Striga hermonthica*; Maize; Methylamine; Trimethylamine

INTRODUCTION

Maize (*Zea mays*) is a cereal crop which belong to the family Graminae is believed to have originated for America which is simply called Corn (Dashak and Shambe, 1993; 2005) America produced 40% of the world harvest among other top producing countries like China, Brazil, Mexico, Indonesia, India and Argentina (Osman *et al.*, 2013). Nigeria 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). Farmers, as recorded in more than 40 countries including semi-arid and tropical areas of Africa, are devastated by the challenge of striga weed (Vassey *et al.*, 2005; Ejeta, 2007; Teka, 2014). This Menace has 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 and others striga species that affect maize (Kim, 1988), 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, 1966; 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% loss of maize and millet in Africa thus compounding the food insecurity problem faced in African countries (Emechebe *et al.*, 2004; Gurney *et al.*, 2006).

Lignocellulosic materials are one of the most abundant renewable resources and natural polymer material (Yang *et al.*, 2011) that have the potential to support large-scale production and nitrification of soil among other fields-fuels, chemicals and polymers (Eriksson *et al.*, 1993). Lignocellulosic materials composed of carbohydrate polymers such as cellulose, hemicellulose, and aromatic polymer lignin (Shambe *et al.*, 1993; Yu *et al.*, 2010; Rowell, 2012; Lee *et al.*, 2014) making it fit for chemical modification since all the component comprises of hydroxyl group. As a soil conditioner, immobilized 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) and 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, while in this work, methylamine and trimethylamine were explored. In recent years, there has been more stress on two aspects of societal importance: utilization of renewable resources to eliminate waste and the use of more environmentally friendly, safe and biodegradable products / waste (Trombetta *et al.* 2010).

This work therefore determine the physical properties of the sawdust, subjecting it to pretreatment using potassium peroxide to convert the exposed hydroxyl group of the lignocellulosic material to carbonyl groups (aldehydes and ketones), treating the oxidised sawdust with methylamine and trimethylamine to effect the immobilization on maize

field and to observe the effect on the crop and striga weed which could solve the problems of farmers.

MATERIALS AND METHODS

Materials

All reagents used were of analar grade and obtained from Zayo limited Jos Plateau State Nigeria. Major equipment include impact sieve shaker (SV003) and Fourier Transformed Infra-Red spectrophotometer (FT-IR P8400S).

Samples collection and treatment

The sawdust 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 5-10 cm depth, was homogenized, air-dried and stored in sealed polythene bags for use in the laboratory. The sawdust sample sizes were distributed by impact sieve shaker (SV003) to obtain 2.00 mm, 1.00 mm and 0.50 mm mesh sizes. Each sieve size particles was collected into a label plastics bags for analysis.

Determination of physiochemical parameter

The physiochemical parameters were analyzed using the following methods or procedures according to (AOAC, 1980). Each treatment of about 1 g 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 1.0 g 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.

Oxidizing the sample

One gram of (1.0 g) of sawdust was treated with various concentrations of potassium periodate (0.02 - 0.1 moldm⁻³) and was allow for 48 hours at 32°C. The samples were severally washed with distilled water after vacuum filtration and were allowed to dry in the oven at 32°C for 24 hours according to Collinson and Thielemans (2010) and Rinaudo (2010). The oxidized

sawdust was used for infrared analysis to study the extent of oxidation.

Immobilization of nitrogenous bases on oxidized sawdust

Methylamine and trimethylamine was incorporated on the oxidized sawdust by weighing about 1.0 g of the oxidized sawdust in 100 mL of 0.5-1.5 moldm⁻³ of each amine. It was then filtered using vacuum filtration after several wash with distilled water and oven dry at 32°C for 24 hours as described by Datta *et al* (2013), Mohamad *et al* (2015) and Rindap *et al* (2017). Infrared analysis was run to study the extent of reaction of the amines into the oxidized sawdust.

Determination of pH

Air dried soil sample size of about 10 g was soaked with 10 mL of distilled water for 10 minutes and allowed to stand for 30 minutes. The pH meter was standardized using pH buffer 7 and 9 and readings were taken after 30 seconds (Wiberg et al., 2001).

Planting of maize seedlings and immobilization on soil

In a 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 sawdust was applied based on the study concentrations and all labeled according to Rindap *et al.*, (2017). The control was also observed.

Fourier transformed infra-red (FT-IR)

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

RESULTS AND DISCUSSION:

Physiochemical Parameter

The results of physiochemical parameters areas represented in Table 1 and Figure 1. The results obtained for *Tectona grandis* lignocellulosic material of various particle sizes in Table 1, deduced that the moisture content increases with increasing particle

sizes having larger particle sizes retaining high moisture as earlier stated by Adhikary *et al* (2008) and Trombetta *et al* (2010). The results also agree that larger particle sizes will be good for this chemical modification since the work is aimed at control release of plant nutrients.

Table 1: Percentage mean moisture and ash contents

Mesh Sizes	0.5 mm	1.0 mm	2.0 mm
% Moisture Content	3.90±0.20	4.20±0.20	4.60±0.10
% Ash Content	2.67±0.06	2.65±0.06	2.64±0.02

Result given as Mean±SEM

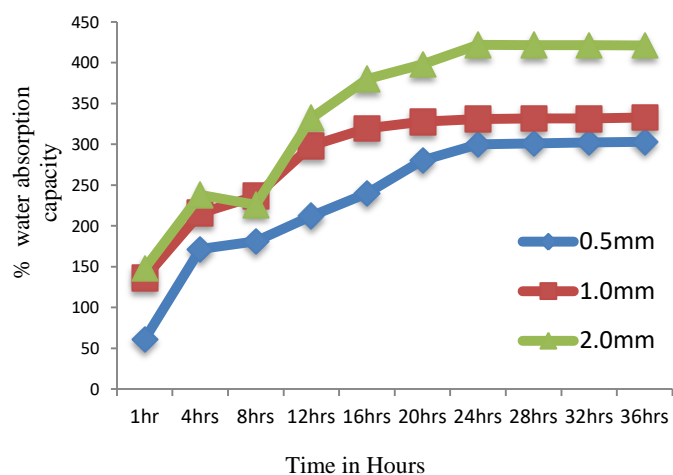


Figure 1: Water absorption capacity of *Tectona grandis* (softwood)

From Figure 1, it is evident that absorption capacity increases linearly with increasing particle sizes and time. This supports the previous works of some colleagues, Clemons (2002), Adhikary *et al* (2008) and Trombetta *et al* (2010) which concluded that it is associated with the surface area, hydrogen bonding of water and the exposed hydroxyl group of cellulose, hemicelluloses and lignin of the supporting material. The high moisture content and water absorption capacity of the sawdust shows that the sawdust can absorb and retain soluble nutrients that can easily be lost because of leaching and with time gradually releases the nutrients for plants since the rate of decomposition of sawdust is very slow (Barbarick, 2014).

The ash content decreases with increase particle size of the sawdust as earlier observed by Demirbas (2004) that a lignocellulosic material with a smaller particle size goes with higher ash content. Showing that the sawdust contains high organic components,

this burns into carbon dioxide (CO₂) and water (H₂O). However, the combustion of untreated biomass has higher organic components than their counterparts (McNamee *et al.*, 2015; Demirbas 2004). This is an evident also that the lignocelluloses material contain reasonable minerals which are useful for plant nutrient and indicating the presence or absence of foreign organic matter such as metallic salt and silica as earlier deduced by David (2014).

The result of the pH value of the soil sample indicated below neutral (4.90 ± 0.10) and therefore considered acidic. Numerous studies have shown that the solubility of elements in the soil is pH dependent. The acidity of the soil (4.90) favors iron (Chuan *et al.*, 1996; Skyllberg, 1999; Iqbal, 2012) but is detrimental to Nitrogen and Potassium; the most needed nutrients for plants (Larsen *et al.*, 2015). In addition, microbial activities are hampered 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 hydrolyse 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).

Infrared spectrophotometric analysis

The infrared results for unoxidized, oxidized and immobilized sawdust are presented in Figures 2-6. The raw sawdust exhibited broadband at 3475.84 and 3373.61 cm⁻¹, which can be attributed to the stretching of O-H groups. These bands indicate high concentration of phenols and alcohols. The intermolecular O-H stretching vibration band of raw sawdust spectrum in the range 3437 cm⁻¹ appeared broader compared to the oxidized sawdust. This could be as a result of KBr encapsulated in the samples by IR runs.

The absorption bands in the region 1749.49 -1729 cm⁻¹ found in 0.02-0.04M KIO₄ oxidized sawdust indicate the presence of carbonyl compounds, carboxylic acids and its derivatives. The dense band of O-H groups by glucose units of the cellulose polymer broadened the peak at 1550-1610 cm⁻¹ which was contributed by C=O bonds. The absorption bands at 2956.01 and 2880.23 cm⁻¹ are due to the C-H stretching of the aldehyde group. Likewise the region

between 1740-1685 cm^{-1} shows C=O stretch for aldehydes and ketones. This region 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).

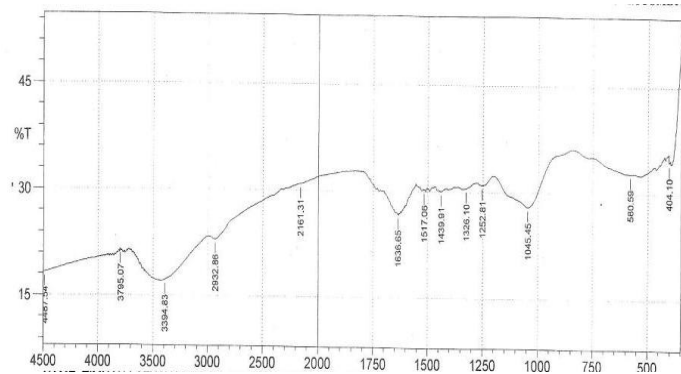


Figure 2: IR spectrum of *Tectona grandis* (Un-oxidized)

to hydrogen bonding between the amides. In addition, the N-H bend at the region 1650.15-1244.13 cm^{-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 1640.15-1244.13 cm^{-1} and C-H stretching at 2960 cm^{-1} – 2860 cm^{-1} are mainly for amides and oximes. All this absorption shows that the amines were attached to the oxidized sawdust (Silverstein *et al.*, 1974; Morrison and Boyd, 1997; Solomon and Fryhle, 2007).

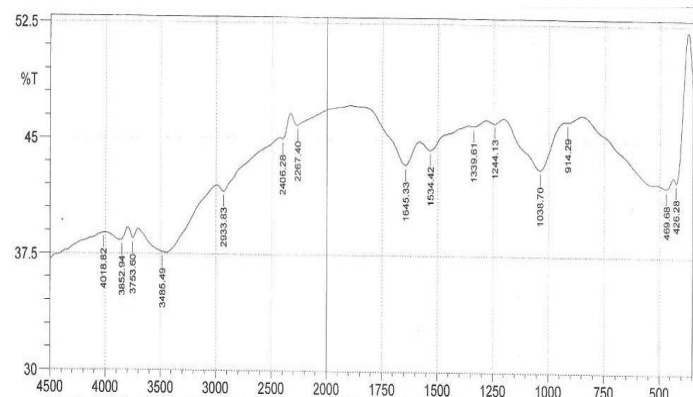


Figure 5: IR spectrum of *Tectona grandis* 0.5M CH_3NH_2

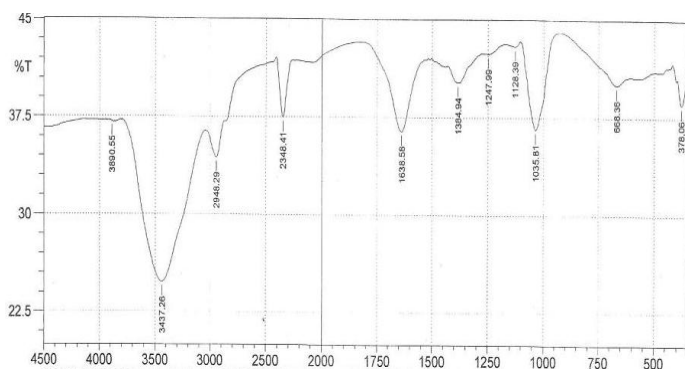


Figure 3: IR spectrum of *Tectona grandis* 0.02M KIO_4

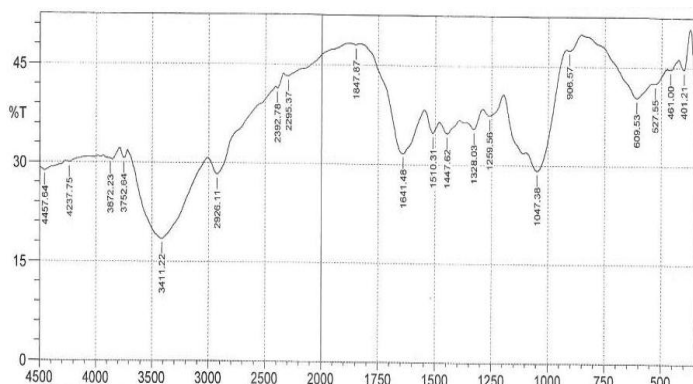


Figure 6: IR spectrum of *Tectona grandis* 0.5M $(\text{CH}_3)_3\text{N}$

Effect of immobilized sawdust on maize and *S. hermonthica*

Incorporated methylamine and trimethylamine sawdust 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

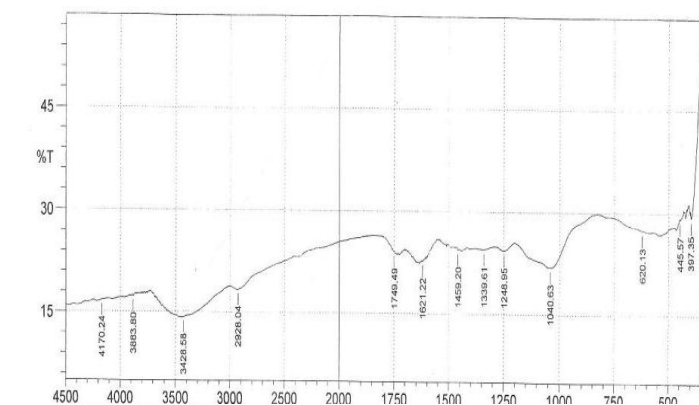


Figure 4: IR spectrum of *Tectona grandis* 0.1M KIO_4

The IR spectra for the immobilized sawdust depicted in Figure 5 and 6, shows that the N–H stretch for amines is between 3493.2-3402.54 cm^{-1} which is due

competition with infested striga as also discussed by Watling and Press (2001) and 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, there was no significant effect on maize and weed due to immobilization as pretreated lignocellulosic materials, both dry and wet, are more hydrophobic than raw counter parts as reported by other researchers (Clemons, 2002; Adhikary *et al.*, 2008; Acharjee *et al.*, 2011)

Nevertheless, on second and third application, there was drastic improvement in maize growth and absent of weeds by gradual decomposition on the soil. On the effect of concentrations of nitrogenous bases, Methylamine immobilized sawdust on Maize grows progressively on 0.5-1.0M and diminished at 1.5M concentration but gradual to complete absence of *S. hermonthica* (Figures 7-10) as earlier observed by Sarmisa (2016) and Rindap *et al* (2017). However, trimethylamine immobilized sawdust on maize grows best at 0.5 mol/dm³ but diminished at 1.0-1.5 mol/dm³ (Figures 11-13). This appears to be due to the tendency of nitrogen to share their pair of electrons available for bonding on primary amine than tertiary amine.



Figure7: Control



Figure 8: 0.5 mol/dm³MA



Figure 9: 1.5 mol/dm³ MA



Figure 10: 1.5 mol/dm³ MA



Figure 11: 0.5 mol/dm³ TMA



Figure12: 1.0 mol/dm³ TMA



Figure 13: 1.5 mol/dm³ TMA

Several studies have shown that nutrients improve crop growth and fertilizers benefit weeds more than crops due to the ability of weeds to accumulate minerals following the application of nutrients to soil. In this case, the nutrients are being control by gradual decomposition of lignocellulosic material to reduce more competitive with maize at higher soil nutrient levels suitable for potential adaptation by farmers for crops productivity and striga control.

CONCLUSION

This study have shown that the application of modified sawdust will help in controlling nutrient leaching and runoff water since it has high water absorption capacity and moisture content. A growing evidence have shown that the solubility of most needed plant nutrients are at higher pH and microbial activities are hampered at low pH, thereby this work have shown that there are potential in the process to correct and harness crop productivity. In addition, concentrations are a factor to consider to effectively using immobilized nitrogenous bases sawdust on maize field and striga weeds.

CONFLICT OF INTEREST

None declared.

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Authors DDA and ARA designed the study, ARA, DDA and DJM wrote the procedures and interpreted the data. Authors ARA and RTL performed the experiments. Authors ARA, DJM and DDA managed the literature searches and produced the initial draft and reviewed the write up for corrections. All authors managed the financial activities.