Acetylation of Violet Tree (*Securidaca longepedunculata*) Root Powder

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Abstract.: The crude violet tree (Securidaca longepedunculata) root powder was modified by acetylation in a solvent free system using acetic anhydride, catalyzed with 4,4,4- cetyltrimethylammonium bromide (CTAB) at a control reaction conditions. The modified Violet Tree Root Powder (VTRP) showed effect of increase weight gain at 50.71 ±0.02%, 63.96 ±0.01%, 64.53 ±0.02%, 75.94 ±0.01%, 78.83 ±0.01% and 96.72 ±0.04% due to varied reaction conditions for temperature, time, acetic anhydride and catalyst concentrations on acetylation. The Fourier Transform Infrared (FTIR) spectral analysis of unmodified and modified VTRP revealed declined frequency band of the hydroxyl group (O-H) of the unmodified 3400 cm1 to 3429-3419 cm1 in modified and consequently the absence of 1750-1700 cm1 in specify samples free of acetic acid by-products.

Keywords: Acetylation, Modification, Sorbent, Violet Tree Root Powder.

1 Introduction

Acetylation (Ethanoylation in IUPAC nomenclature) describes a reaction that introduces an acetyl (CH_3CO) functional group into a chemical compound (Encarta, 2009). It is one of the most significant reactions for the derivatization or modification of cellulose and its allied lignocelluloses (Bogan *et al*., 1979, Pizzi *et al*., 1994). Consequently, cellulose acetate is one of the most important cellulose derivatives because of its broad applications, in textiles, plastic film, packaging, and cigarette filter row (Hon *et al.*, 1996)

Acetylation has been the most widely used successful chemical modification. It is a single site reaction that replaces a hydroxyl group with an acetyl group (Xu & Sun, 2003). Acetyl groups are more hydrophobic than hydroxyl groups; therefore, replacing some of the hydroxyl groups reduces the hydrophilic property of the cell wall polymers (Rowell, 1992). The acetyl group is also larger than the hydroxyl group therefore, the materials undergoes permanent expansion (Karr & Sun, 2002). In general, acetylation leads to an increased content of acetyl groups in the wood material, to approximately 20 % weight compared with 1-2 % weight for unmodified wood. The introduction of new acetyl groups in wood Polymers results in a certain degree of bulking of the wood cells walls. This, in combination with the decreased ability to attract water molecules leads to highly improved dimensional stability of acetylated wood material (Brelid & Simonson, 1999).

Modification with acetic anhydride can substitute the hydroxyl groups of cell wall polymers from these vegetable products with acetyl groups; mean while improves the properties of these polymers so that they become hydrophobic. These modified absorbents have the characteristics of low cost, high capacity and quick oil uptake and are easy to desorb by a simple squeezing method (Sun *et. al,* 2003). Nwankwere *et al.*, (2011) in their study of thermal and dimensional stability of catalyzed acetylated rice husks, showed that the slight change in thermal strength of the rice husk was due to the replacement of accessible hydroxyl (OH) group in its matrix with the acetyl group. Thus, an evident of successful acetylation using N-bromosuccinimide, therefore it is feasible and useful to improve the dimensional stability of lignocellulose compounds.

The Lignocelluloses fiber can be modified by physical and chemical methods as described by Malkapuram *et al.*,(2009). Physical methods, such as stretching, calendaring, thermo-treatment, and the production of hybrid yarns do not change the chemical compositions of the fibers. Physical method of treatment changes structural and surface properties of fiber and thereby influences the mechanical bonding to polymers (Malkapuram *et al*., 2009).

Chemical method involves the direct modification carried out to attained adequate structural durability and efficient sorption capacity by sorbent (Kamel *et al*., 2006). It is also used to vary certain properties of the components of agricultural residues, such as cellulose. It's hydrophilic or hydrophobic characters, elasticity, water sorbency, adsorption or ion-exchange capability, resistance to microbiological attack, and thermal resistance (McDowell *et al*., 1984). The hydroxyl groups are the main functional groups in the agricultural residues. Functional groups may be attached to this hydroxyl groups by variety of chemistries. The principle and main routes of direct hydroxyl groups' modification in preparation of adsorbent materials are esterification, etherification, halogenation, oxidation and chemical grafting modification (O'Connell *et al.*, 2008).

The plant violet tree is botanically called *Securidaca longepedunculata* from the family *Polygalaceae*. It is commonly known as Sanya or Uwar Magunguna (as related in English Mother of Medicine), Wild Wistaria or Rhodes Violet in South Africa. It is found in the Northern and Southern Nigeria, known as Ipeta among the Yoruba's, Alali among the Fulani's; some Africans refer to it as Muteya or Mziyi in Swahili, Saagat or Alali in Arabic. It is a semi deciduous shrub or small tree that grows to 12 metres tall, with often flattened or slightly fluted bole. It is spiny and much branched, with an open, rather straggly looking crown. It is widespread through the tropical Africa (Orwa *et al.*, 2009).

The plant is of wide medicinal applications among Africans (Orwa *et al*., 2009). The Mbula people in Adamawa State of North Eastern Nigeria chewed the root among selves to reconciled kinsmen. The plant known as *"Ngbann"* among the people is believed to have mysterious cleansing over grudges internally felt to avert any unfortunate incidence between aggrieved persons. Roots are worm as a charm against witch craft and protection against snakes in Nigeria. It is also a natural surfactant, thus can wash and bleach cloth as reported by Agu (2010). The aim of this study is to develop a hydrophobic modified violet tree root powder (MVTRP) that could be used in further sorption studies.

2 Materials and methods

Acetic anhydride, cetyltrimethylammonium bromide, ethanol, acetone, VTRP sample.

The plant Violet Tree Root was sourced from Girei town of Adamawa State-Nigeria. The plant was dug from the ground of about 2-3 cm depth using a hoe. The roots were cut from the plant stem with knife, washed with distilled water and spread on a polyethene bag to dry in the laboratory. Subsequently, it was cut into pieces and crushed to powder form using piston and mortar. The grinded powder was sieved using 0.66 um into fine powder of Violet Tree Root Powder (VTRP) particles and kept in a clean plastic container with tight cover labelled VTRP Sample. All reagents used were analytical grade obtained from BDH with no further purifications carried out.

2.1 Acetylation of VTRP

The acetylation of violet tree root powder (VTRP) was carried out under mild conditions, in the presence of Cetyltrimethylammonium bromide (CTAB), using acetic anhydride as indicated by Sun *et al.,* (2004) method of acetylation in a solvent free system with little changes. 15 g of VTRP was placed in a 500 ml flat bottom flask containing 300 cm^3 of acetic anhydride and 30 g of Cetyltrimethylammonium bromide. The flask was put into a thermostatic water bath set at 100 ℃ under atmospheric pressure, with a reflux condenser fitted. The flask was then removed and the hot reagent decanted off after 3 hours. The acetylated VTRP was thoroughly washed with ethanol and acetone to removed unreacted acetic acid by-product. The new product was oven dried at 60 ℃ for 8 hours. The dried modified VTRP was re-weighed to determine the weight gained on the basis of initial oven dry measurement. The weight percent gain (WPG) of the VTRP due to acetylation was calculated from:

$$WPG = \text{weight gain/original weight} \times 100$$

2.2 Fourier transform infrared (FTIR) spectrophotometer analysis

The unmodified and modified VTRP samples were characterized by FTIR using KBr plates over spectral range of 4000-400 cm^1 with a resolution of 4 cm^1 and presented without baseline correction or normalization, to conclude whether a chemical reaction took place between the VTRP sample and acetic anhydride. The FTIR spectra were detailed by Shimatzu (FTIR-8400) Fourier Transform Infrared Spectrometer at National Research Institute for Chemical Technology (NARICT) Zaria- Nigeria.

3 Results and discussion.

3.1 Effect of Acetic Anhydride and Catalyst on VTRP Acetylation.

The profile of the acetylation of VTRP using different concentrations of acetic anhydride and catalyst are shown in Figure 1 and 2. The solid to liquid ratio observed at 1:10, 1:15, 1:20, and 1:30 of sorbent to acetic anhydride mixture resulted to increment at 50.71 ±0.01%, 64.53 ±0.02%, 75.94 ±0.01%, 78.83 ±0.01% and 96.72 ±0.04% accordingly. Obviously, the structural modification by introducing acetyl groups in place of the accessible hydrogen atoms of the hydroxyl group is apparent with increased weight gain and specified FTIR analysis discussed later. The modification improvement by Cetyltrimethylammonium bromide (CTAB) catalyst dosage from 1% - 3%, respectively, have shown efficient acetylation, catalyzed with CTAB as obtained by Sun *et al.*, (2004) and Bodirlau and Teaca (2007) in modified lignocellulose. The optimum weight percent gain due to catalyst concentration was recorded at 2.5% and 3% as 78.83 ±0.01% and 96.72 ±0.04%

respectively. Thus, the use of CTAB in acetylation does not only speed up the rate of hydroxyl group bond breaking by brominated mediated catalysis, but also its advantageous position of removing hemicellulose components of the organic material, which is highly responsible for the sorbent hydrophilicity is significant. This study agrees with similar findings by Bledzki *et al.*, (2008) on the effect of acetylation on properties of flax fibre, which established increased in catalyst concentration between 0.026 % and 0.052 % yielded 40 % and 45 % weight increases in acetylated products of the flax fibre. Thus, increasing the concentration of catalyst facilitates the rates of depositions of desired changes consequently increasing the weights of product. Hence, this research priority of modification of VTRP has unfolded a new modified fiber product that could have improved hydrophobic sorbent capacity as desired in the used of acetylation process.

The acetylation profile of VTRP using different concentration of acetic anhydride are shown in Figure 1 and 2

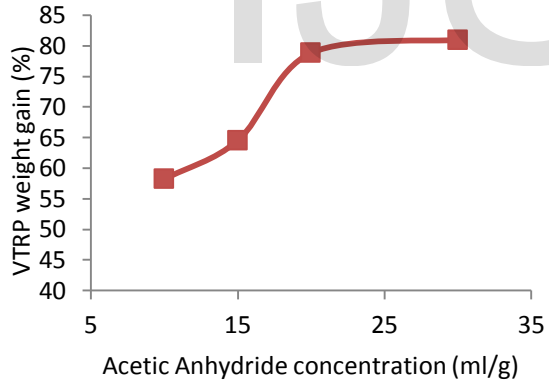

Figure:1 Effect of acetic anhydride on acetylation of VTRP.

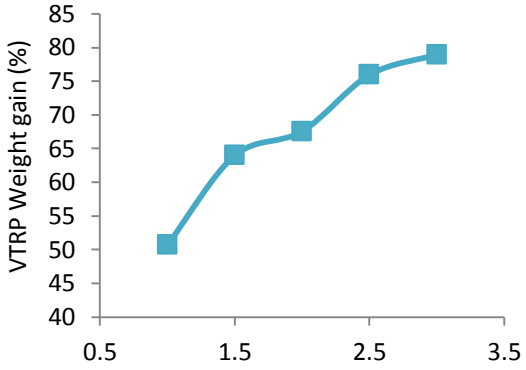

Figure: 2 Effect of catalyst (CTAB) on acetylation of VTRP.

3.2 Effect of Time on Acetylation of VTRP

The weight percent gain (WPG) increased along the reaction time from 1h - 3h respectively as can be seen in Figure 3. However, the reaction time at 3h gave the optimum weight gain of 68.11%; which was later chosen for further evaluation. According to Faraham and Taghizadeh (2010), the esterification with higher WPG increases all fiber parameters significantly. Thus, the WPG was an indication of effective treatment that improves the desired properties of modified VTRP sorbent for further applications.

Though, there was subsequent decrease in the weight gain, after the reaction time of 3h at the 3½h, 4h, 4½h, and 5h acetylation, there was a decreased from 51.96 %, 53.87 %, 54.27 % and 50.98 %. Perhaps, it may be due to de-acetylation that lignocellulose materials experience with increasing reaction time as put forward by Adebajo and Frost (2004) in the acetylation of raw cotton materials using 4-dimethylaminopyordine (DMAP) as catalyst.

Furthermore, the effect of acetylation and de-acetylation mechanisms, the complications in the variation of the level of acetylation (WPG) with reaction time and catalyst concentration may also be as a result of complex matrix of organic materials. Jayanta and Kale (2008) showed that rice husk, apart from cellulose which is the major component of rice husks with more than 35 %, lignin 20 %, hemicellulose 25 % and silica ash about 17 % by weight were other components present. Hence, the

hydrophilic nature of fiber materials is evident by the hydroxyl group of hemicellulose that can be reinforced.

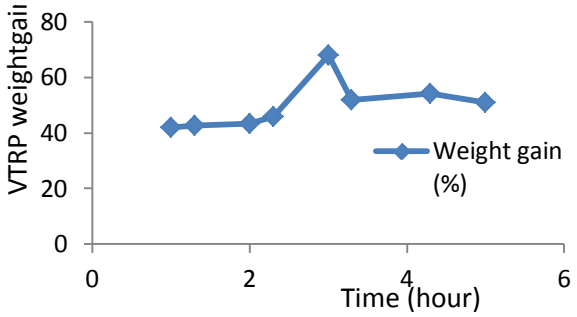

Figure 3 Effect of time on acetylation of VTRP

3.3 Effect of Temperature on Acetylation of VTRP .

The acetylation condition due to temperature increased in this work has led to higher weight gain by the VTRP.

Sun *et al.*, (2003) pointed out that reaction temperature plays an important role on the effect of acetylation. In present research, the percentage weight gain increased with raised in temperature which is as indication of an effective acetylation. As illustrated in Figure 4. the temperature increase from 30 – 100℃ was responsible for the weight percent gain due to acetylation at 54.84 %, 78.09 %, 86.54 %, 95 % and 96.72 % respectively. This result also agreed with Nwankwere (2011), where acetylated rice husk showed increased weight gain with increasing temperature during modification.

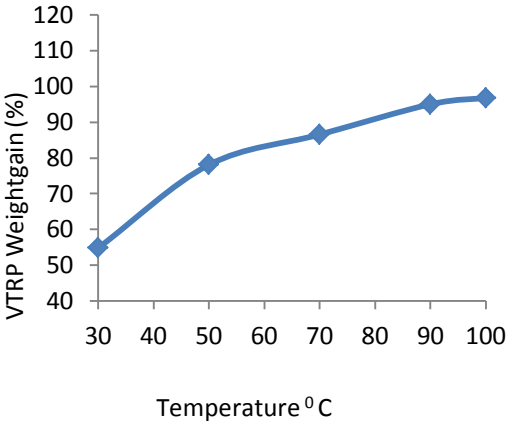

Figure:14 Effect of temperature on Acetylation of VTRP.

3.4 Fourier Transform Infrared Spectrophotometer analysis.

The subsequent Fourier Transform infrared spectroscopy (FT-IR) revealed acetylation reaction to be successful. The enhanced O−H (Hydroxyl group) stretching absorption, C=O ester stretching and C−O− stretching bands decreased frequency of 3429−3263 cm^{-1}, also presence of C=C absorption at 1645 cm^{-1} and 2922 cm^{-1}, was a confirmation of the ester bonds formed. The C−O stretching enhanced at 1651 cm^{-1} and 1354−1359 $cm^{-1}$of C−H bond in $–O(C=O)–CH_3$ group. Interestingly, the absence of absorption bands O-H bonds at 1730−1700 cm^{-1} was an indication of effective modification and the advantageous effect of the catalyst CTAB. These spectral changes are as shown in Figure 5, 6, 7, 8, and 9.

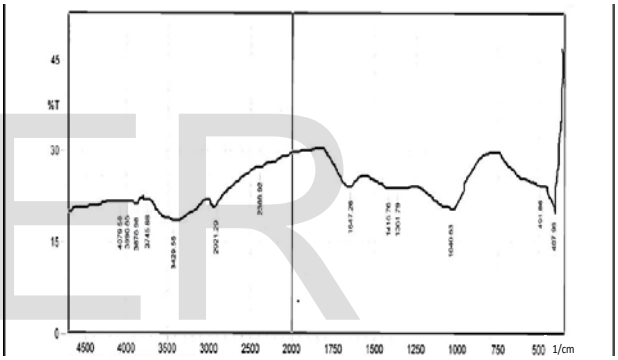

Figure 5: FTIR of unmodified VTRP

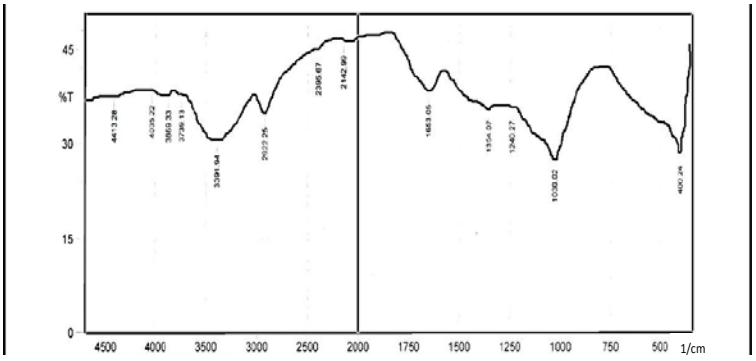

Figure 6: FTIR of modified VTRP 1

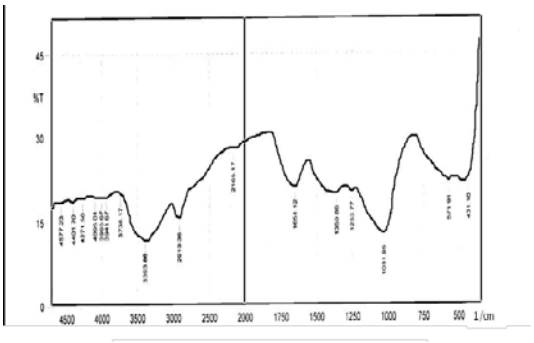

Figure 7: FTIR of modified VTRP 2

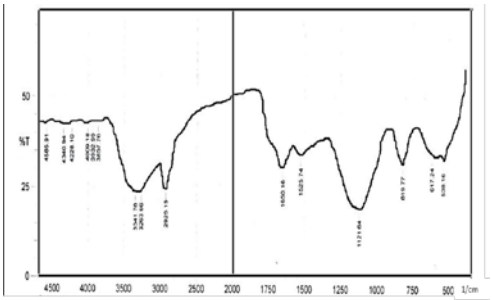

Figure 8: FTIR of modified VTRP 3

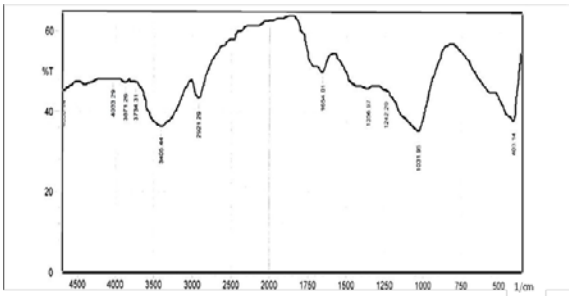

Figure 9: FTIR of modified VTRP

4 Conclusion

The acetylation reaction in the presence of cetyltrimethylammonium bromide (CTAB) as catalyst was successful and effective. The result revealed optimum acetylation at 3 hours with weight gain increased between 50.71 % - 96.72 % using 1-3 % catalyst concentrations along increase reaction time between 1-5 hours respectively. The partial acetylation recorded in shifting of hydroxyl band at 3429-3419 cm^{1} also, achieved the research purpose to modify the sample into more hydrophobic material.

REFERENCES

Adebajo, M.O., & Frost, R.L., (2004) Acetylation of raw cotton for oil spill cleanup application an FTIR and 13C-MAS NMR Spectroscopic investigation, spectrochimica Acta, part A molecular and bio-molecular spectroscopy, 60, (10) pp. 2315-2321.

Agu Mathew O. (2010). Unpublished Thesis. Evaluation of some properties of violet plant (*Securidaca longepedunculata*) root as surfactant. Presented to graduate school, school of pure and applied science Federal University of Technology, Yola.

Bledzki A, K., Mamun A.A., & Lucka-Gabor M. (2008). The effect of acetylation on

properties flax fibre and its polypropylene composites. Vol. 2, NO.6 pp. 413-422

Bogan, R.T., Kuo, C.M., & Brewer R.J. (1979). in encyclopedia of chemical Technology , Vol. 5, 3RD Ed., H.F Mark, D.F Othmer, C.G.Overberger and G.T Seaborg, Eds., Willey Interscience, New York 703-756.

Brelid, P.L., & Simonson, R., (1999). Acetylation of solid wood using microwave heating, part II: Werkst. 57, 383-389.

Bodirlau, R., & Teaca., C.A (2007). Fourier transform infrared spectroscopy and thermal analysis of lignocellulose fibers treated with organic anhydrides. Romanian Journal of Physics, Bucharest. 54 (1-2) pp 93-104.

Encarta (2009). Microsoft student, Redmond, W.A Microsoft Corporation.

Farahan, M.R.M., & Taghizadeh, F.,(2010). Roughness of esterified estern Cottonwood, bioresources 5,(4) Pp.2232-2238.

Hon, D.N.S., Lie-Gui, T., & Yu-Qin, Z., (1996). An investigation in solution acetylation of cellulose by microscopic techniques. Solution Acetylation of Cellulose. John Willey & Sons, Inc. pp 1953-1960.

Jayanta, B & Kale, D.D (2008).Properties of polypropylene of filled with chemically treated rice husk. Journal of Applied Polymer Science,110:1271-1279.

Kamel, S., Hassan, E.M., & Halligan, J. (2006). Removal of oil from water surfaces by sorption on unstructured fibers., Environ Sci. Technol. 7 (5), 439-443

Karr, G.S., & Sun, X.Z., (2002). Straw board from vapour phase acetylation of wheat straw. Ind crops prod. 11pp 31-41.

Malkapuram Ramakrishna , Vivek Kumar & Yuvraj Singh Negi (2009). Recent development in natural fiber reinforced polypropylene composites. Journal of Reinforced Plastics and Composites. Vol. 28 No. 10. Pp 1169-1177

McDowall, D.J Gupta, B.S & Stannett, V.T (1984). Grafting of Vinyl monomers to cellulose by ceric ion initiation, prog. polym-sci. 10, 1-50.

Nwankwere,E.T., Omolaoye J.A, Nwadiogbu J.O & Nale B.Y (2011). Thermal and dimensional stability of NBS catalyzed acetylated rice husks. Der chemica sinica 2 (1) pp 189-195. Available at http://www.pelagiaresearchlibrary.com

O'connell D.W., Birkinshaw, C., & O'Dayer, T.F (2008). Heavy metal adsorbents prepared from modification of cellulose : A review bioresource technol 99: 6709-672

Orwa, C., Mutua, A., Kindt, R., Jamnadass, R., & Simons, A. (2009). Agro-forestry database, A tree reference ad selection guide version, available at 4.0 http://www.worldagroforestry.org/af/treedb.html

Pizzi.,A Stephanou, A Boonstra, M.J & Pendirburg A.J .(1994). Holzforschung 48,91-94.

Rowell, R.M. (1992). Opportunities for lignocellosic materials and composites. AGS Symp ser 476 12p 12-27

Sun, X. F. Sun, R.C. & Sun, J.X.(2003). Acetylation of rice straw with or without catalyst and its characterization as a natural sorbent in oil spill cleanup., J. Agric food chem, 50 (22), 6428-6433.

Sun, X.F. Sun, R.C. Sun, J.X. & Zhu Q. K. (2004). Effect of tertiary ammine catalyst on the acetylation of wheat straw for the production of oil sorption-active materials C.R. Chim 7: 125-134.

Xu. F., & Sun R.C. (2003).The chemically modified cereal straw as efficient sorbents in oil spill clean up. Journal of Cellulose Science Technology (11) 51-56