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THE EFFECT OF SILVER SALTS ON THE PROPERTIES OF SUGARCANE BAGASSE CELLULOSE

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ABSTRACT

In this study, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FT-IR) methods were used to study the structure and the thermal degradation of the cellulose modified with silver nitrate, silver sulphate and silver borate. The absorption of the nitrate derivative is more intense followed by the borate. All the cellulose derivatives showed two degradation steps, except for bromate derivatives which indicated the third peak that is related to a nature and chemistry of a derivative presence. The modification seems competent for an application for modified fillers in polymer composites.

KEYWORDS: Silver nitrate, silver borate, silver sulphate, cellulose derivatives.

INTRODUCTION

Sugarcane bagasse (SCB) is a byproduct of the sugar production industry, it consists of cellulose 43%, hemicellulose 33.8%, lignin 18.1%, ash 2.3% and wax 0.8% on a dry weight basis (Sun et al. 2004). A ton of sugarcane generates 280 kg of bagasse during sugar extraction, and approximately 583 dry tons of sugarcane are processed annually throughout the world (Cerqueira et al. 2007). On the other hand about 50% of sugarcane bagasse is used in distillery plants as a source of energy (Pandey et al. 2000, Pattra et al. 2008). Sugarcane bagasse has also been found useful in the biofiltration technology. It has been found that sugarcane bagasse could actually be effective and cheap alternative packing material for biofiltration systems in the removal of benzene vapor from gaseous streams (Sene et al. 2002, Adsul et al. 2004).

Lignocellulosic materials from different crop residues have been used for conversion to ethanol. One of the major lignocellulosic materials found in great quantities to be considered, especially in tropical countries, is sugarcane bagasse (SCB), the fibrous residue obtained after extracting the juice from sugar cane (*Saccharum officinarum*) in the sugar production process

(Monteiro et al. 1998). Its abundant of lignocellulose makes it possible to yield fermentable sugars for the production of lactic acid after hydrolysis. Sugarcane bagasse is used in the biological production of fuel ethanol because it is cheaper and more abundant, therefore reducing the cost of feedstock (Cardona and Sánchez 2007). The hydrolysis of lignocellulosic materials from sugarcane bagasse mostly produces hydrolysates which are fermentable sugars such as xylose, glucose and arabinose. It also produces some soluble materials namely lignin, acetic acid and furfural that can inhibit both growth and sugar utilization of microorganisms during the fermentation process (Aguilar et al. 2002, Sibiya et al. 2018).

Cellulose has particular significance owing to its unique structure and distinct tendency to form intra- and intermolecular bonding. These characteristics influence the cellulose supramolecular arrangement that together with other practical aspects such as the product origin and processing treatment, have important consequences on the final properties of cellulose nanoparticles can be easily extracted from naturally occurring biomass via a mechanical or chemical route. The source of the cellulosic material and the conditions under which the hydrolysis is performed is very important for the varying of geometrical dimensions (length, L, and width, w) of CNCs. Cellulose nanocrystals show a notable decrease in dimensions and an increase in crystallinity when the hydrolysis time is increased. With excessive increase in the hydrolysis time and temperature, degradation of the CNCs is observed.

Although there are some reports of raw sugarcane bagasse as the adsorbent, however, owing to its low adsorption capacity, there is a need to explore some simple means of chemical modification to enhance its metal adsorption properties.

Therefore, because of the importance of SCB as an industrial waste, there is great interest in developing methods for the biological production of fuel and chemicals that offer economic, environmental, and strategic advantages (Adsul et al. 2004). Bio composites consisting of the polymer matrix and natural cellulose fibers are environmentally-friendly materials which can replace glass fibre-reinforced polymer composites, and are currently used in a wide range of fields such as the automotive and construction industries, electronic components, sports and leisure (Pereira et al. 2015).

In the approximately 80 sugarcane producing countries there is a potential to make better use of the SCB. Subjected to improved energy efficiency, sugar producers could supply energy either as co-generated electricity, or as fuel ethanol through cellulose hydrolysis followed by fermentation (Botha and Blottnitz 2006, Pattra et al. 2008). The most common use for SCB is the energy production by combustion (Ramjeawon 2008). In addition, SCB can be used also to produce chemical compounds such as furfural or hydroxymethylfurfural (Almazán et al. 2001), paper paste (Pattra et al. 2008) or ethanol (Laser et al. 2002). The use of SCB in chemistry and biotechnology has been reviewed elsewhere (Pandey et al. 2000). As raw material, SCB should be analyzed from composition, structure and surface properties. SCB is primarily composed of lignin (20–30%), cellulose (40–45%) and hemicelluloses (30–35%) (Peng et al. 2009). Because of its lower ash content, 1.9%, bagasse offers numerous advantages compared with other agro-based residues such as paddy straw, 16% (Goh et al. 2009), rice straw, 14.5% (Guo et al. 2009) and wheat straw, 9.2% (Monteiro et al. 1998) studied the possible uses of bagasse waste as reinforcement in polyester matrix composites. Preliminary results have attested this possibility. Composites with homogeneous microstructures could be fabricated and the levels of their mechanical properties enable them to have practical applications similar to the ones normally associated with wooden agglomerates

From previous researches, to the best of our knowledge, little is known or nothing whatsoever about the effect of different silver solutions on the chemical and physical properties of the final sugarcane bagasse cellulose derivatives. The current study explores the systematic comparison of solutions and the possible properties for resulting cellulose derivatives (Krishnaraj et al. 2010).

MATERIAL AND METHODS

Materials

Sugar cane bagasse, with cellulose, hemicellulose, lignin and ashes ranging from 32 - 44%, 27 - 32%, 19 - 24% and 4.5 - 9% respectively, was supplied by Tongaat Hullet in Empangeni area. Silver nitrate (assay 99.2%), silver bromate (assay 99.0%) and silver sulphate (assay 98.5%) were purchased form Sigma-Aldrich.

Methodology

Sugarcane cellulose was collected, readily available from previous experiments. Salts of silver nitrate, silver bromate and silver sulphate were used to make three different solutions of silver. One molar of each silver salts prepared in 500 ml volumetric flask with distilled water. Amount of 30 g of sugarcane cellulose was submerged in each solution for 72 hours using a beaker. The untreated cellulose was only submerged in distilled water as a control. The beakers were heated at 70°C for 2 hours and were stirred after every 30 min. After cooling, the cellulose derivatives were washed several times with distilled water to PH neutral before drying at 50°C for 24 hours.

Characterization techniques

Fourier transmission infrared spectroscopy (FTIR)

FT-IR spectroscopy analysis was carried out on a Bruker Tensor 27 FT-IR spectrometer using a standard ATR cell; the catalysts were analysed as-synthesised with no prior preparation required. The force was adjusted to 90 gauges for sufficient contact between the surfaces. The catalysts were scanned over the mid-IR region (450- 4000 cm^{-1}).

Powder X-ray diffraction (XRD)

The XRD characterization of all samples was performed on Powder X-Ray diffraction spectroscopy (Bruker AXS Advance D8 diffractometer) with monochromatic CuKα(λ=1.5406 Å) incident radiation at 40 kV and 40 mA at room temperature. The samples were scanned within the high angle 2θ range to get all characteristic diffractions of the materials at 0.5 scan speed and 0.01314 increments.

Thermal gravimetric analysis (TGA)

Thermogravimetric analyses were performed using TGA analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 ml·min^{-1}. Approximately 10-15 mg of sample was heated from 25°C to 600°C at a heating rates rate of 10°C·min^{-1}. The sample weight loss and rate of weight loss were recorded continuously as functions of temperature. The analysis was only started when isothermal condition had been obtained.

RESULTS AND DISCUSSIONS

Optical Microscopy

Fig. 1 showed microscope images of cellulose (A) at 200 μm magnification, the suspensions treated with silver nitrate (B), silver sulphate (C) and silver borate (D). Cellulose looks whiter than the rest followed by nitrated cellulose. Borated and sulphated are darker than the rest and have what appeared as clusters ranging from about 150 to 300 μm randomly dispersed. The clusters are arguably visible in sulphated cellulose yet smaller, but almost invisible in cellulose.

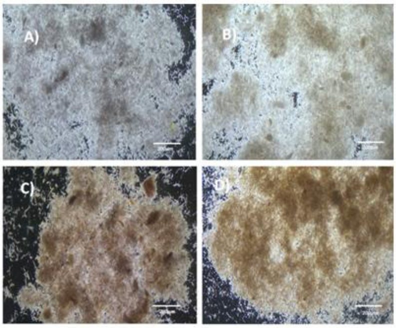

Fig. 1: Optical microscopy of cellulose (A), the suspensions treated with silver nitrate (B), silver sulphate (C) and silver borate (D).

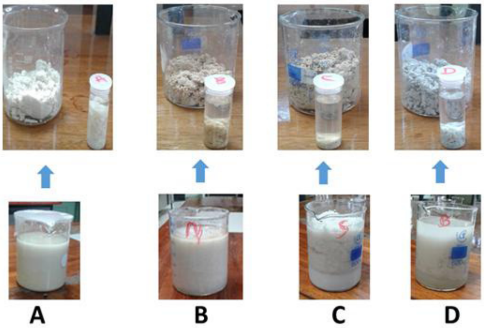

Fig. 2: Images of cellulose (A), the suspensions treated with silver nitrate (B), silver sulphate (C) and silver borate (D).

Figure showed that the treated cellulose is generally less milky than the untreated. Intense color changes were observed during the heating dominated by yellowish to brownish which is known for the presence of silver nanoparticles (Krishnaraj et al. 2010). The borate suspension instead was light grayish. It is known in literature that formation of cellulose derivatives is normally accompanied by color changes (Granström et al. 2009). The observations are supported by images in Fig. 2.

FTIR Spectroscopy

The FTIR spectra for untreated suspension of cellulose, the suspensions treated with silver nitrate, silver sulphate and silver borate studied are shown in Fig. 3.

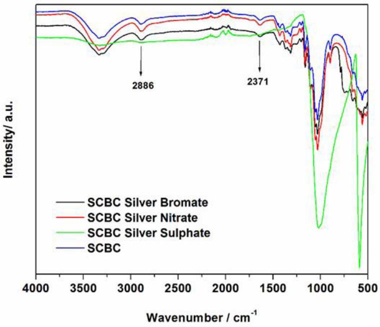

Fig. 3: FTIR of cellulose (A), the suspensions treated with silver nitrate (B), Silver sulphate (C) and silver borate (D).

In most of the curves the OH stretching modes around 3400 cm^{-1} and another two bands at around 2920 and 2850 cm^{-1}, related to asymmetric and symmetric methyl and methylene stretching group are present, except for the derivative from sulphate suspension which showed almost nothing at the OH region. In the fingerprint region, the bands at 1595, 1510 and 1270 cm^{-1} are assigned to C=C, C–O stretching or bending vibrations of different groups present in lignin (Granström et al. 2009). However, these bands are almost invisible in the peak of suphate cellulose derivative. That could practically imply the total elimination of the remaining lignin or the formation of derivatives with less aromatic structures relative to the rest.

XRD Diffraction

The X-ray diffractograms of cellulose, the suspensions treated with silver nitrate, silver sulphate and silver borate studied are shown in Fig. 4. Following the order of sharpness of the peaks the sulphate derivative appeared more crystalline followed bromate derivatives, untreated cellulose, nitrate and respectively. Logically it would be expected that the untreated cellulose would have greater crystallinity due to aggressive breakage of long range order resulted from chemical treatments (Granström et al. 2009, Linganiso et al. 2019). Nonetheless, the explanation, in this study, seems to be limited when coming to nitrate and bromate derivatives. As for sulphate derivative it seemed as though most of the amorphous cellulose region interacted strongly with sulphate ion to form more crystalline structure than the rest. Another possibility which could not be ruled out is the dissolution and/or re-crystallization of amorphous cellulose by sulphate ions (Granström et al. 2009). These results could be another back up explanation for the disappearance of aromatic structures in FTIR.

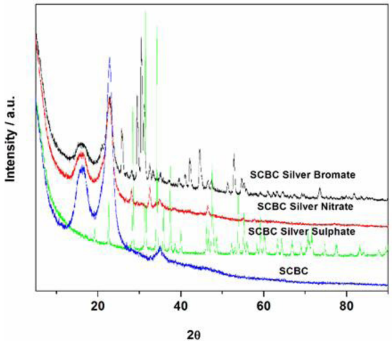

Fig. 4: XRD of cellulose (A), the suspensions treated with silver nitrate (B), Silver sulphate (C) and silver borate (D).

Ultraviolet–visible spectroscopy

The UV curve of cellulose, the suspensions treated with silver nitrate, silver sulphate and silver borate studied are shown in Fig. 5.

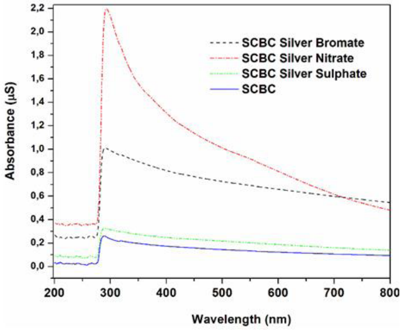

Fig. 5: UV absorption of cellulose (A), the suspensions treated with silver nitrate (B), Silver sulphate (C) and silver borate (D).

The UV absorbance of the conjugated C=C bond of both untreated and treated cellulose clearly have maxima at approximately 290 nm, but for the nitrate derivative the maxima has slightly shifted to 295 nm. In fact, the absorption of the nitrate derivative is more intense followed by the borate. Interestingly sulphate derivative and untreated cellulose appeared to have similar absorption and the maxima. The decrease in intensity might signify different interactions of OH from cellulose with different functional groups as estimated by FTIR and XRD.

Thermogravimetric analysis

Fig. 6 represents the thermal stability of untreated cellulose, the suspensions treated with silver nitrate, silver sulphate and silver borate. All the peaks showed two degradation steps, except for bromate derivatives which their interaction with cellulose leads to the third peak. Sulphate cellulose derivative appeared to be more thermally stable than all the samples trailed by untreated cellulose, nitrated and bromate derivatives. In addition, sulphate derivative displayed most char content trailed by bromate, when untreated cellulose and nitrate derivatives almost share the similar residue weight. These transitions are related to degradation mechanism followed by a cellulose derivative (Granström et al. 2009, Laser et al. 2010). In fact, it is safe to mention that bromate and sulphate derivatives seems to follow different and independent degradation mechanism, while untreated and nitrate seems to follow similar route which lead inconsistencies in char content, if it had to be expected whatsoever.

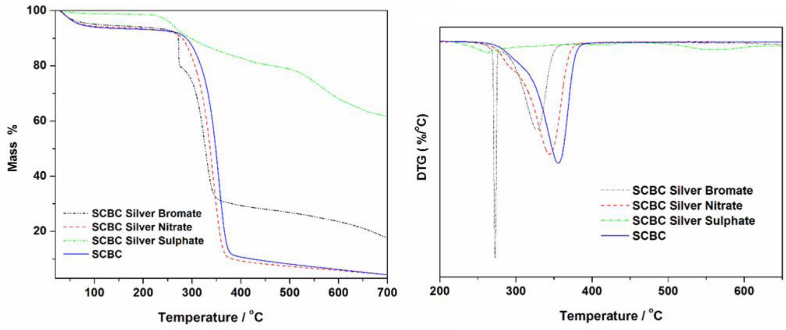

Fig. 6: TGA and DTG absorption of cellulose (A), the suspensions treated with silver nitrate (B), Silver sulphate (C) and silver borate (D).

CONCLUSIONS

The preparation and characterizations of cellulose derivatives were successfully prepared. The treatment of sugarcane bagasse cellulose with different silver salts had obviously shown different effects on the characteristics of the final cellulose. Color change and different cluster sizes were the main highlights of the results trailed by the competing thermal stabilities, from which the borate derivative revealed dominance. It should be noticed that the absorption appeared to be governed by OH interaction or replacement on the cellulose surface. That led, if it has to bedeviled, to the dominance of nitrate derivative be followed by the borate when sulphate derivative and untreated cellulose appeared to have similar absorption and the maxima.

REFERENCES

1. Adsul, M.G., Ghule, J.E., Singh, R., Shaikh, H., Bastawde, K.B., Gokhale, D.V., Varma, A.J., 2004: Polysaccharides from bagasse: applications in cellulase and xylanase production. Carbohydrate Polymer 57: 67-72.

2. Aguilar, R., Ramírez, J.A., Garrote, G., Vázquez, M., 2002: Kinetic study of acid hydrolysis of sugarcane bagasse. Journal of Food Engineering 55: 309-318.
3. Almazán, O., González, L., Gálvez, L., 2001: The sugarcane, its byproducts and coproducts. Sugar Cane International 7: 3–8.
4. Botha, T., Blottnitz, H.V., 2006: A comparison of the environmental benefits of bagasse-derived electricity and fuel ethanol on a life-cycle basis. Energy Policy 34: 2654-2661.
5. Cardona, C.A., Sánchez, O.J., 2007: Fuel ethanol production: process design trends and integration opportunities. Bioresource Technology 98: 2415–2457.
6. Cerqueira, D.A., Rodrigues, G., Meireles, C.D., 2007: Optimization of sugarcane bagasse cellulose acetylation. Carbohydrate Polymers 69: 579-582.
7. Goh, C.S., Tan, K.T., Lee, K.T., Bhatia, S., 2009: Bio-ethanol from lignocellulose: status, perspectives and challenges in Malaysia. Bioresource Technology 101: 4834-4841.
8. Guo, G.L., Hsu, D.C., Chen, W.H., Chen, W.H., Hwang, W.S., 2009: Characterization of enzymatic saccharification for acid-pretreated lignocellulosic materials with different lignin composition. Enzyme and Microbial Technology 45: 80-87.
9. Granström, M., 2009: Cellulose derivatives: Synthesis, properties and applications. Laboratory of Organic Chemistry Department of Chemistry Faculty of Science University of Helsinki Finland. Academic dissertation. Helsinki University Printing House, Helsinky, 119 pp.
10. Krishnaraj, C., Jagan, E.G., Rajasekar, S., Selvakumar, P., Kalaichelvan, P.T., Mohan, N., 2010: Synthesis of silver nanoparticles using *Acalypha indica* leaf extracts and its antibacterial activity against water borne pathogens. Colloids and Surfaces B Biointerfaces 76: 50-56.
11. Laser, M., Schulman, D., Allen, S.G., Lichwa, J., Antal, M.J., Lynd, L.R., 2002: A comparison of liquid hot water and steam pretreatments of sugar cane bagasse for bioconversion to ethanol. Bioresource Technology 81: 33-44.
12. Linganiso, L.Z., Buthelezi ,T., Motaung ,T.E., 2019: A comparative study of sugarcane bagasse and soft wood. Wood Research 64: 273-28.
13. Monteiro, S.N., Rodriquez, R.J.S., De Souza, M.V., d'Almeida, J.R.M., 1998: Sugar cane bagasse waste as reinforcement in low cost composites. Advanced Performance Materials 5: 183-191.
14. Pandey, A., Soccol, C.R., Nigam, P., Soccol, V.T., 2000: Biotechnological potential of agro-industrial residues, I. Sugarcane bagasse. Bioresource Technology 74: 69-80.
15. Pattra, S., Sangyoka, S., Boonmee, M., Reungsang, A., 2008: Bio-hydrogen production from the fermentation of sugarcane bagasse hydrolysate by *Clostridium butyricum*. International Journal of Hydrogen Energy 33: 5256-5265.
16. Peng, F., Ren, J.L., Xu, F., Bian, J., Peng, P., Sun, R.C., 2009: Comparative study of hemicelluloses obtained by graded ethanol precipitation from sugarcane bagasse. Journal of Agricultural and Food Chemistry 57: 6305-6317.
17. Pereira, P.H.F., Rosa, M.D.F., Cioffi, M.O.H., Benini, K.C.C.D.C., Milanese, A.C., Voorwald, H.J.C. and Mulinari, D.R., 2015: Vegetal fibers in polymeric composites: a review. Polímeros 25: 9-22.
18. Ramjeawon, T., 2008: Life cycle assessment of electricity generation from bagasse in Mauritius. Journal of Cleaner Products 16: 1727-1734.
19. Sun, J.X., Sun, X.F., Zhao, H., Sun, R.C., 2004: Isolation and characterization of cellulose from sugarcane bagasse. Polymer Degradation and Stability 84: 331-339.
20. Sibiya, N.N., Mochane, M.J., Motaung, T.E., Linganiso, L.Z., Hlangothi, S.P., 2018: Morphology and properties of sugarcane bagasse cellulose- natural rubber composites. Wood Research 63: 821-832.

21. Sene, L., Converti, A., Felipe, M.G.A., Zilli, M., 2002: Sugarcane bagasse as alternative packing material for biofiltration of benzene polluted gaseous streams: a preliminary study. Bioresource Technology 83: 153-157.

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