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CHARACTERIZATION AND EVALUATION OF DRUG DELIVERY POTENTIAL OF CELLULOSE MICROCRYSTALS OBTAINED FROM CORNCOB (*ZEA MAYS*) AND SUGARCANE BAGASSE (*SACCHARUM OFFICINARIUM*)

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ABSTRACT

Cellulose has attracted worldwide attention as a renewable raw material for producing many industrial materials including medicines. Cellulose has been produced from various synthetic and natural sources, including a few agricultural wastes. Cellulose materials in their small particle sizes offer delivery of potential drugs via specialized drug delivery systems. This study aims at producing cellulose microcrystals from two agricultural wastes; corncob (*Zea mays*) and sugarcane bagasse (*Saccharum officinarium*) and evaluating the extracted cellulose for drug delivery potentials. Cellulose was extracted from corncob (CC) and sugarcane bagasse (SB) by alkaline extraction followed by a delignification and bleaching process. The powders obtained were characterized using physicochemical parameters such as surface morphology, swelling index, flow properties, densities, particle size analysis, pH, moisture content, viscosities, and Fourier Transform Intra-Red (FT-IR) Spectra. The Cellulose was hydrolyzed by Sulphuric acid using varying hydrolytic conditions (60%$^{v}/_{v}$ and 65% $^{v}/_{v}$ acid for 45 and 90 minutes at a constant temperature of 45°C). The hydrolytic reaction was quenched with deionized water. The hydrolyzed cellulose particles were washed, centrifuged at least six times, and oven-dried at 30°C, and were evaluated using FT-IR spectroscopy, scanning electron microscopy (SEM), and pH measurements. The cellulose with good physicochemical properties was extracted from both corncob and sugarcane bagasse at high yields with potential for use in the design of drug delivery systems. Hydrolysis of the extracted cellulose produced materials of reduced particle size on the micro-scale.

KEYWORDS: Cellulose, Cellulose microparticles, Corncob, Sugarcane bagasse, Drug delivery systems.

INTRODUCTION

Drugs formulated in preparations or medicines, rather than as pure chemical substances, usually contain one or more drugs (active substances) and/or other formulation additives such as excipients, solvents, stabilizers, etc. to make them more appropriate and convenient for use and for target-specific delivery.[1] Pharmaceutical excipients may be obtained from nature through plants, animals, minerals, and agricultural wastes which when properly employed can modify dosage forms to the benefit of the formulation scientists and the intended users.

A drug delivery system is a formulation or a device that allows for introducing an active therapeutic substance into the body and improves the drug's safety and efficacy by controlled release of the drugs in the body.[2]

Nanoparticles could be employed as a means to deliver therapeutic agents to specific targeted body sites in a controlled manner. These materials offer numerous benefits in the treatment of diseases by site-specific and target-oriented delivery of precise medicines.[3] These nanoparticles for controlled drug delivery can be metallic, organic, inorganic, and polymeric materials, including natural polysaccharides, peptides, liposomes, dendrimers, and micelles. They are selected based on the physicochemical characteristics of drugs and in particular those drugs with poor solubility and less absorption. Their efficacy as drug delivery systems varies and is dependent on the shape, size, and other inherent biophysical and biochemical properties.[3] In 1838, a French Chemist, Anselme Payne obtained a substance that was not starch (sugar or glucose but which still could be broken down into its basic unit of glucose just as starch. He named the new substance "cellulose" because he obtained it from the cell walls of plants.

Cellulose and its derivatives are utilized extensively as drug delivery systems due to their green, natural, and unique binding and encapsulation properties.[4] Cellulose is an outstanding naturally occurring biopolymer with distinctive structural properties. It is the world's most abundant polymer in nature and is an important structural component of the cell wall of various plants.[5] A wide

variety of living organisms such as plants, bacteria, fungi, algae, and tunicates (marine creatures) are composed of cellulose. Cellulose is a major renewable source of materials.[6] The wide range of applications of cellulose can also be attributed to the ability of cellulose materials to self-assemble into well-defined structures in multiple scales.[7]

Cellulose has a wide range of applications and offers several advantages as drug delivery excipients due to their smaller size, biocompatibility, hydrophilicity,[5] low cost, inertness, biodegradability[8] and availability.[9] They have good mechanical properties, high aspect ratio, low density, unique optical properties, low thermal expansion, low toxicity and surfaces that can be chemically modified easily due to the presence of hydroxyl groups.[7] Common chemical modifications can be accomplished by reactions such as esterification, etherification, amidation, carbamation, nucleophilic substitution,[5] oxidation, sulfonation, cationization, silylation and grafting by means of acid anhydride, acid chloride or isocyanate.[10]

Cellulose based materials have been studied in recent years due to their flexibility in regard to chemical modifications, physical properties and their wide range of applications.[11] In the cell walls of plants, approximately thirty-six (36) individual cellulose molecular chains connect through hydrogen bonds to form larger units called elementary fibrils. These fibrils are a promising raw material due to their high mechanical strength, stiffness, large surface area, low thermal expansion, optical transparency, renewability, biodegradability, low cost, and low toxicity.[6]

Cellulose materials with a high degree of crystallinity are produced when the amorphous regions of cellulose are selectively hydrolyzed under certain condition.[6] Acid hydrolysis is well-known and widely used for the extraction of cellulose crystals from a wide variety of sources because of the moderate operation conditions required and the good stability of the resulting suspensions.[6] Strong mineral acids that break the disordered (amorphous/non-crystalline) regions of the pure cellulose fibre to release single and well-defined cellulose crystals include sulphuric acid, hydrochloric acid, phosphoric acid, hydrobromic acid, and nitric acid.[12] Cellulose crystals are produced by breaking down cellulose fibres and isolating the crystalline regions by strong acid hydrolysis[13] as the crystalline regions are insoluble in the acids under the reaction conditions.[14] The morphology and properties of the cellulose microcrystals depend on the source of the cellulosic substrate and hydrolysis process conditions.[15]

Sulphuric acid treatment at a concentration between 60-70%[9] is the most effective and widely used extraction method. Materials produced by this method have been reported to be either rod-shaped (more common) or spherical, have birefringent gels, and liquid crystallinity, and are helicoidally self-arranged within certain concentration ranges.[16]

The morphology (size, shape, crystallinity, etc.) and other properties of the cellulose obtained vary considerably from one source to another. Cellulose can be sourced naturally which includes plant, animal, or mineral sources, or synthetically such as from petrochemicals. Agricultural waste is an important natural source of cellulose; cellulose has been obtained from corn stalks, rice straw, and wheat straw.[17] This study considered obtaining cellulose from two different agricultural wastes; corn cob and sugar cane bagasse.

Corn cob is the central part of an ear of corn on which the grains are attached. Corn, also called maize (*Zea mays* L., Family: Poaceae), is a cereal crop widely grown in every continent except Antarctica.[18] It is a primary food source and a stable raw material for the production of starch and starch-based industrial products.[18] Corn is one of the important cereal crops grown and is accompanied by an enormous amount of agro-waste generation; corn cob constitutes 30% of this agro-waste.[19] Corn cobs are potential feedstock for producing heat, power, fuels, and chemicals.[20] The cobs are mainly used in animal feed and fertilizer production, however, they are used industrially to produce furfural and other chemicals such as xylose.[14]

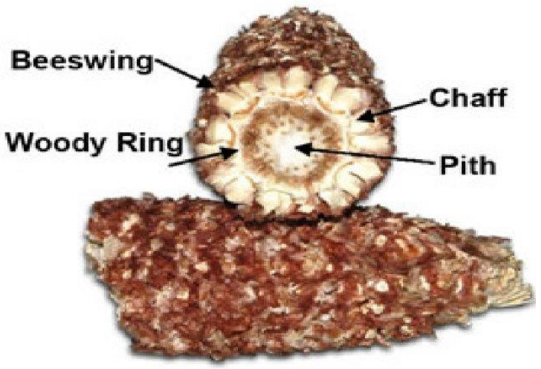


Fig. 1: The Corn cob: Retrieved from: https://www.resarchgate.net/publication/282499528-Production of lignin peroxidase by Ganoderma leucidum using solid state fermentation/figures. October 20, 2019.

Corn cob, an abundantly available annual fibre crop, is composed of 38.8% ± 2.5% cellulose, 44.4% ± 5.2% hemicellulose (mainly xylan composed of xylose and arabinose), 11.9% ± 2.3% lignin and other components such as starch, fat, protein, and ash.[21]

Corn cobs being lignocellulosic materials are an important cellulosic source to obtain cellulose nanocrystals by acid hydrolysis.[14] Cellulose obtained from corn cob has numerous application potentials as pharmaceutical and biomedical materials, biosensors, drug delivery agents, and polymer reinforcement agents and can be used in the textile, automotive, cosmetics,

painting, aerospace, electrical, and electronic industries[22][7] used the cellulose nanoparticles obtained from corn cob as a colon-specific drug delivery agent while[14] applied cellulose nanocrystals from corn cob as reinforcing agents in nanocomposites.

Sugarcane bagasse is the fibre that remains after the juice has been extracted during sugarcane (*Saccharum officinarum* L., Family: Poaceae) processing. The Composition of Sugarcane bagasse by weight is cellulose (40-50%), hemicellulose (25-35%), and lignin (17-20%).[23] Other components of sugarcane bagasse include pectin, waxes, proteins, fats, and other inorganic contaminants. Most of the cellulose in sugarcane bagasse is in a crystalline structure.[24] Sugarcane bagasse, an abundantly available agro-waste, is a promising source of biomass and can be used to produce a great number of value-added products such as pellets, electricity, and ethanol. Paperboard, and specialty chemicals such as vanillin.[25]

As a result of its high cellulose content, sugarcane bagasse is a good raw material for synthesizing cellulose nanocrystals by acid hydrolysis with improved physical, chemical, and mechanical properties. The cellulose nanocrystals isolated from sugarcane bagasse can be applied in various ways to produce better and more useful products such as protective coatings, supercapacitors, substrates for electronics and lithium batteries, organic solar cells, nanocomposite reinforcing agents, nanofillers for polymers, filtration systems, and separation membranes.[7]

Sugarcane bagasse and corn cob are regarded as wastes and are discarded indiscriminately in spite of the rich cellulose contents and renewability.

This study therefore aimed to extract and characterize cellulose obtained from two agricultural wastes; corn cob and sugar cane bagasse. The extracted cellulose will further be subjected to acid hydrolysis and evaluated for drug delivery potential.

MATERIALS AND METHODS

Materials

The materials used include bare corncobs and sugarcane stalks (obtained from the Oja-Oba market in Ibadan, Oyo State, Nigeria). All reagents used were of analytical grade.

Methods

Extraction of Cellulose from Corn Cob

The corn cobs were air-dried and milled using a domestic grinder (Panasonic MX-AC400 Mixer Grinder, MX-AC400, India). The particles obtained were weighed and stored in an air-tight container. The powdered corn cobs were delignified in a 3%$^{w}/_{v}$ solution of sodium hydroxide with mechanical stirring at 100°C for 3 hours using the Corning Magnetic Stirrer with Heater. The mixture was allowed to cool after which the supernatant was decanted and the resultant residue was strained through a clean calico sieve cloth. The residue was then washed free of the alkaline with distilled water until neutrality; washing was done for about 6 to 8 times. The residue was strained to remove the excess water present and was allowed to dry in an air-circulating oven (Gallenkamp BS oven 250 size 1, Leicestershire, UK) for 24 hours at 50°C. The weight of the residue was noted before milling in a domestic grinder. The delignified corn cobs were then bleached in a solution containing sodium hypochlorite (0.02g per gram of corn cob) at 80°C for 2 hours. The mixture was then allowed to cool, the supernatant was decanted and the resultant residue was then washed free of the alkaline until neutrality with distilled water about 6 to 8 times. The residue was strained through a clean calico sieve cloth to remove the excess water present. The neutrality of the residue was confirmed with the aid of an indicator paper and it was then placed in an air-circulating oven for 24 hours at 50°C. The dried residue (cellulose) was then stored at room temperature in an air-tight container.[26]

Extraction of Cellulose from Sugarcane Bagasse

The sugarcane stalks were peeled, and crushed and the juice was extracted using a clean sieve cloth. The bagasse was then air-dried for four days after which it was pulverised. The powder obtained was weighed and stored in an air-tight container. The milled sugarcane bagasse was dewaxed using petroleum ether-ethanol (mass ratio, 1:1) as the extraction solvent in a soxhlet apparatus and allowed to air dry for 24 hours. The dewaxed bagasse was then treated with distilled water at 55°C for about 2 hours to remove the water soluble contents. The mixture was filtered and the residue was delignified with acidified sodium chlorite solution (1.3% $^{w}/_{v}$ sodium chlorite in 10% $^{v}/_{v}$ acetic acid) at 75°C for about 1 hour. The delignified bagasse obtained was then treated with 10% $^{w}/_{v}$ potassium hydroxide and 10% $^{w}/_{v}$ sodium hydroxide at 20°C for about 1 hour. The mixture was then filtered and washed carefully with distilled water and 95% $^{v}/_{v}$ ethanol and the resultant residue (cellulose) was placed in an air-circulating oven for about 20 hours at 50°C. The dried cellulose was then stored in an air-tight container at room temperature.[6]

Characterization of the Extracted Cellulose

Photomicrography

The corn cob and sugar cane bagasse celluloses were examined under an optical microscope (Olympus Optical Co, Japan). The size and shape of the materials were noted. Photomicrographs were taken at the ×40 magnifications only.

Swelling Index

Approximately 2 g of the cellulose powders obtained from the corn cob and sugarcane bagasse were each weighed into measuring cylinders. The initial volumes (V_o) occupied by each cellulose powder were determined and recorded. The powders were then dispersed in distilled water and the volume was made up to 50 mL

with distilled water. The mixtures in the cylinders were left to stand for 24 hours after which the volume of the sediment (V_s) was measured and recorded. The swelling index was then calculated using the equation.

$$Swelling\ Index = Vs / Vo \quad (1)$$

Where: V_o = Initial powder volume before dispersion
V_s = Volume of sediment after 24 hours
Determinations were carried out in triplicates.

Angle of Repose

Approximately 10 g each of the cellulose powders were poured through a short stem funnel clamped on a retort stand into an open-ended glass cylinder with a round cork of radius, r, at its base. The cylinder was removed vertically thus allowing the powder to flow out and cascade into a heap. The height of the resultant cone formed was measured using a pair of dividers and a ruler. The angle formed between the slant height of the cone and its horizontal base is the angle of repose (θ). The angle of repose (θ) was calculated using the equation.

$$Tan\,\theta = h/r \quad (2)$$

Where: h = Height of the powder heap (cone)
r = Radius of circular base
The mean value of three determinations was calculated.

Flow Rate

The flow rate was determined by weighing 5 g of each cellulose powder into a short stem funnel closed off with a stopper. The powder was then allowed to flow through the funnel and the time (t) taken for all of the powder to flow out was recorded. The flow rate was calculated using the formula:

$$Flow\ Rate = \frac{Weight\ of\ the\ powder\ in\ gram}{Flow\ Time\ (t)} \quad (3)$$

The flow rate was determined in triplicates and the mean value was calculated.

Moisture Content

The moisture contents of the cellulose powders of corn cob and sugarcane bagasse were determined on 2 g samples of the powders using a moisture analyser (AND MX-50) with super hybrid sensor (SHS).

Density Measurements

The Bulk and Tapped densities of the cellulose powders of corn cob and sugarcane bagasse were determined on 10 g samples of each powder. The powder was poured into a 50 mL measuring cylinder through a funnel and the volume occupied by the powder was noted. The Bulk density was determined as the ratio of the mass of the powder (M_p) to the volume occupied by the powder (V_p). The tapped density was determined by applying 100 taps at uniform intervals to exactly 10 g of the powder in a measuring cylinder and the volume occupied by the powder was noted. The tapped density was recorded as the ratio of the mass of the powder (M_p) to the volume occupied by the powder after tapping (V_{pT}).

$$Bulk\ Density = \frac{Mass\ of\ Powder\ (Mp)}{Powder\ Volume\ (Vp)} \quad (4)$$

$$Tapped\ Density = \frac{Mass\ of\ Powder\ (Mp)}{Tapped\ Volume\ (VpT)} \quad (5)$$

Determinations were carried out in triplicates.

Carr's Compressibility Index

The Carr's compressibility index is used to evaluate the flow properties of powders. The Bulk and Tapped densities were used to calculate the Carr's Index of the cellulose powders of corn con and sugarcane bagasse using formula:

$$Carr's\ Index = \frac{Tapped\ density - Bulk\ Density}{Tapped\ Density} \times 100 \quad (6)$$

Hausner's ratio

The Bulk and tapped densities were used to calculate Hausner's ratio of the cellulose powders:

$$Hausner's\ Ratio = \frac{Tapped\ Density}{Bulk\ Density} \quad (7)$$

Particle Density

The true densities of the cellulose powders of corn cob and sugarcane bagasse were determined using the solvent pycnometer method with xylene as the non-solvent. (Ayorinde et al., 2019) The weight of the empty 50ml capacity pycnometer (W) was recorded. It was then filled with the non-solvent (xylene) and the excess was wiped off. The weight of the pycnometer and the non-solvent (W_1) was then determined. The difference in the weight was calculated as W_2. Exactly 2g of the cellulose powder of the corn cob was weighed (W_3) and transferred into the pycnometer bottle with the aid of a funnel. The excess non-solvent was wiped off the pycnometer and weighed again (W_4). The particle density was then calculated using the equation.

$$\frac{W_2 . W_3}{50(W_3 - W_4 + W_2 + W)} gcm^{-3} \quad (8)$$

The determination was done in triplicates and the mean value was noted.

PH Determination

A 2% $^{w}/_{v}$ aqueous slurry of each of the celluloses of corn cob and sugarcane bagasse were prepared and the pH of the resultant mixture was determined using a pH meter (720A, Thermo Electron Corporation, MA, USA).

Viscosity

The viscosity of 2% $^{w}/_{v}$ aqueous slurry of the celluloses was determined using a Brookfield Rheometer (DV-III + model, Brookfield Engineering, USA) and using spindle size 3 and speeds of 20, 50, and 100 rpm.

Particle Size Analysis
Pre-cleaned sieves (2000µm, 1180µm, 500µm, 360µm, 200µm, and 75 µm) were weighed and arranged vertically in order of decreasing mesh sizes on the receiver and placed on the mechanical sieve shaker. The dried cellulose powders were then weighed and placed on the top sieve and the lid was replaced. The sieves were then subjected to shaking for 10 minutes, after which they were disassembled and the powders retained on each sieve (including the receiver) were weighed and recorded.

Fourier Transform Infrared (FT-IR) Spectroscopy
The cellulose powders were analyzed by FT-IR (FT-IR Spectrum BX II by PerkinElmer, Waltham, MA, USA) in transmission mode. The transmission spectra range was 4000 - 400 cm^{-1} using 64 scans with resolution of 8 cm^{-1}.

Isolation of Cellulose Nanocrystals from the cellulose Powder
Sulphuric acid hydrolysis was used to cleave the glycosidic bonds in the cellulose powders with constant stirring. The acid concentration and reaction time were varied while keeping the temperature constant; treatment conditions of 60 and 65 % acid concentrations and reaction times of 45 and 90 minutes were used to obtain samples A1, A2, A3,A4, B1, B2, B3 and B4. The acid to powder ratio used for the isolation was 20 mL: 1 g. The cellulose powders used were in the size range of 200µm. The reaction was terminated with deionized water. Mixture of the hydrolysed solution and deionized water (1:10) was centrifuged at least six times at 10,000 rpm for 15 minutes, the supernatant was decanted, filtered and washed with deionized water until the pH remained unchanged after which the particles were obtained by oven drying in an air-circulating oven. The yield of the isolation process was then calculated.[7]

Evaluation of the Hydrolysed Cellulose
Fourier Transform Infrared (FT-IR) Spectroscopy
In order to detect any alteration in functional groups of the extracted cellulose and the hydrolyzed cellulose, the FT-IR spectra of the hydrolyzed materials were compared with spectra of the cellulose powders respectively obtained from corn cob and sugarcane bagasse.

PH Determination
An aqueous slurry of 1% $^{w}/_{v}$ of the hydrolyzed cellulose of corn cob and sugarcane bagasse were prepared and the pH of the resultant mixture was determined using a pH meter (720A, Thermo Electron Corporation, MA, USA).

Scanning Electron Microscopy (SEM)
The size, shape, and surface morphology of the cellulose microparticles were observed using scanning electron microscope JEOL JSM-6060LV (Tokyo, Japan) at 5.0kV. The cellulose microparticles were mounted on aluminum stubs with double-sided carbon tape attached to each stub and coated with a gold film under vacuum in a sputter coater and observed.

RRESULTS AND DISCUSION
Yields
The yield of cellulose obtained from the extraction of corncob was 41.1%w/w while that obtained from sugarcane bagasse was 43.24%w/w.

The yield of cellulose materials obtained from corn cob and sugarcane bagasse celluloses are presented in Table I.

Particle Size Analysis
The size distribution of the cellulose powders of corn cob and sugarcane bagasse are shown in Tables 11 and III respectively.

Photomicrographs of the cellulose of corncob and sugarcane bagasse are shown in Figures 1 and 2 respectively. A bar chart showing the distribution of the particle diameter is presented in Figure 3.

Physicochemical Properties of Cellulose Powders
The physicochemical properties of the cellulose powders of corncob and sugarcane bagasse are presented in Tables IV. The FT-IR spectroscopy of the cellulose powders of corn cob and sugarcane bagasse are presented in Figures 4 and 5 respectively while the FT-IR spectroscopy of the hydrolysed cellulose micro-particles of corn cob and sugarcane bagasse are presented in Figure 6.

Scanning Electron Microscopy (SEM)
The Scanning Electron Micrographs of the hydrolyzed cellulose microparticles are presented in Figures 7 and 8 respectively.

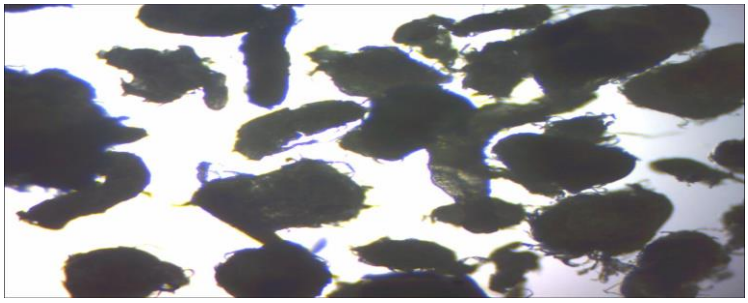


Figure 1: Photomicrograph of Corn Cob Cellulose (×40).

Figure 2: Photomicrograph of Sugarcane Bagasse Cellulose (×40).

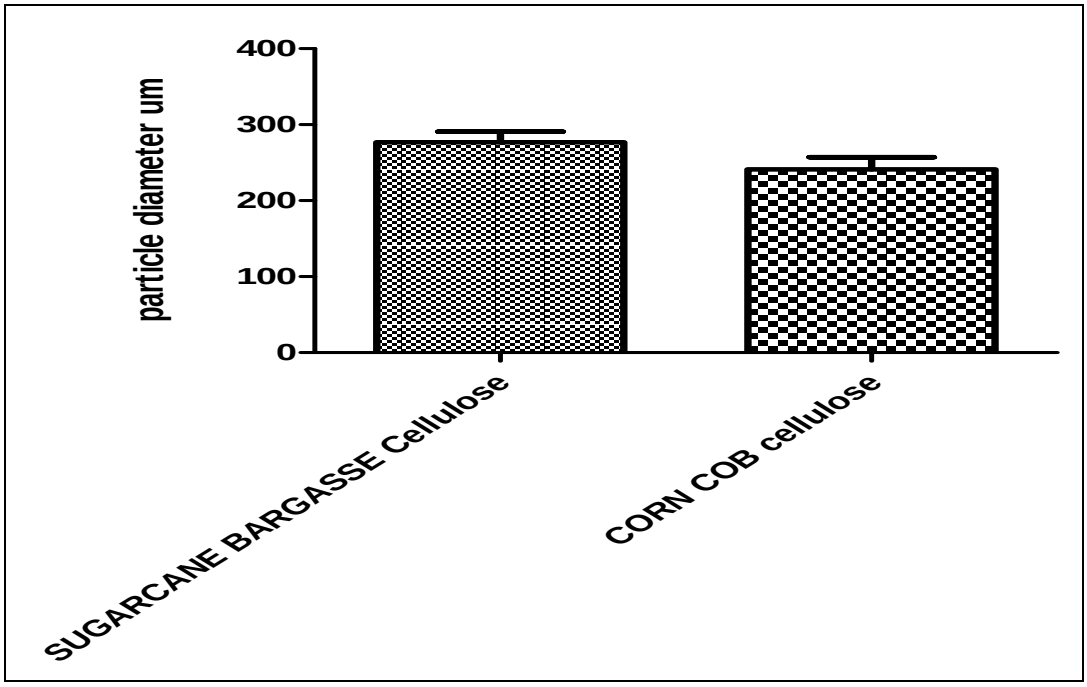


Figure 3: Measured statistics of the Particle diameter of the Cellulose powders.

Table I: The yield and pH of the cellulose nanoparticles obtained from corncob and sugarcane bagasse at different treatment conditions.

Sample	Acid Concentration (%)	Reaction Time (minute)	Yield (%$^{w}/_{w}$)	pH
A1	60	45	52.41	3.30
A2	60	90	40.21	3.08
A3	65	45	40.07	3.03
A4	65	90	37.21	3.05
B1	60	45	80.10	3.32
B2	60	90	38.31	3.26
B3	65	45	85.03	3.47
B4	65	90	43.31	3.78

Table II: Particle size analysis of the cellulose powder obtained from corncob using sieve method.

Sieve Mesh Size	Weight of Cellulose Retained (g)	Percentage Retained (%)	Cumulative Percentage Retained (%)
2.0 mm	0.02	0.02	0.021
1.18 mm	4.14	4.64	4.66
500 µm	36.71	41.19	45.85
360 µm	5.11	5.72	51.57
200 µm	39.13	43.90	95.47
75 µm	0.47	0.53	96.00
0 µm	3.21	3.60	99.60

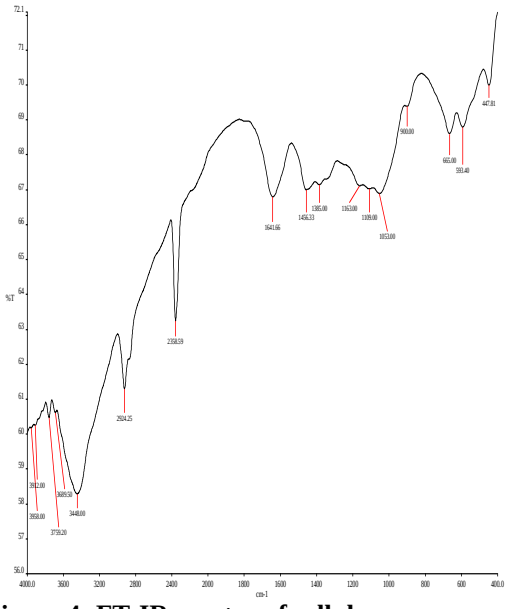
Table III: Particle size analysis of the cellulose powder obtained from sugarcane bagasse using sieve method.

Sieve Mesh Size	Weight of Cellulose Retained (g)	Percentage Retained (%)	Cumulative Percentage Retained (%)
2.0 mm	0.64	1.81	1.81
1.18 mm	7.92	22.38	24.19
500 µm	6.08	17.18	41.37
360 µm	1.21	3.42	44.79
200 µm	18.89	53.38	98.17
75 µm	0.29	0.82	98.99
0 µm	0.76	2.15	101.14

Table IV: Physicochemical properties of the cellulose powders obtained from corn cob and sugarcane bagasse.

Physicochemical Properties	Corn cob Cellulose	Sugarcane Bagasse Cellulose
Swelling Index	1.30	1.14
Angle of Repose (°)	36.29	19.08
Flow Rate (g/sec)	0.12	0.74
Moisture Content (%)	12.27	9.32
Bulk Density (gcm^{-3})	0.43	0.22
Tapped Density (gcm^{-3})	0.49	0.25
Carr's Index (%)	12.77	10.43
Hausner's Ratio	1.15	1.12
Ph	6.23	6.19
Particle Density (gcm^{-3})	1.335	1.255
Viscosity (cp)	8.00	19.00

Mead ± SD (n = 3)



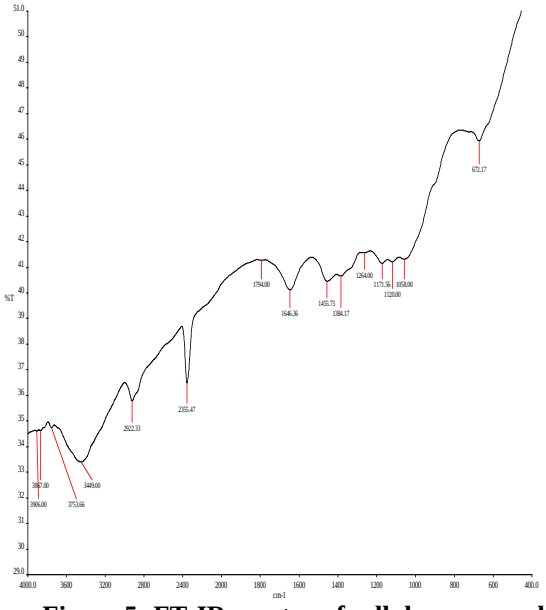


Figure 4: FT-IR spectra of cellulose sugarcane bagasse. Figure 5: FT-IR spectra of cellulose corn cob.

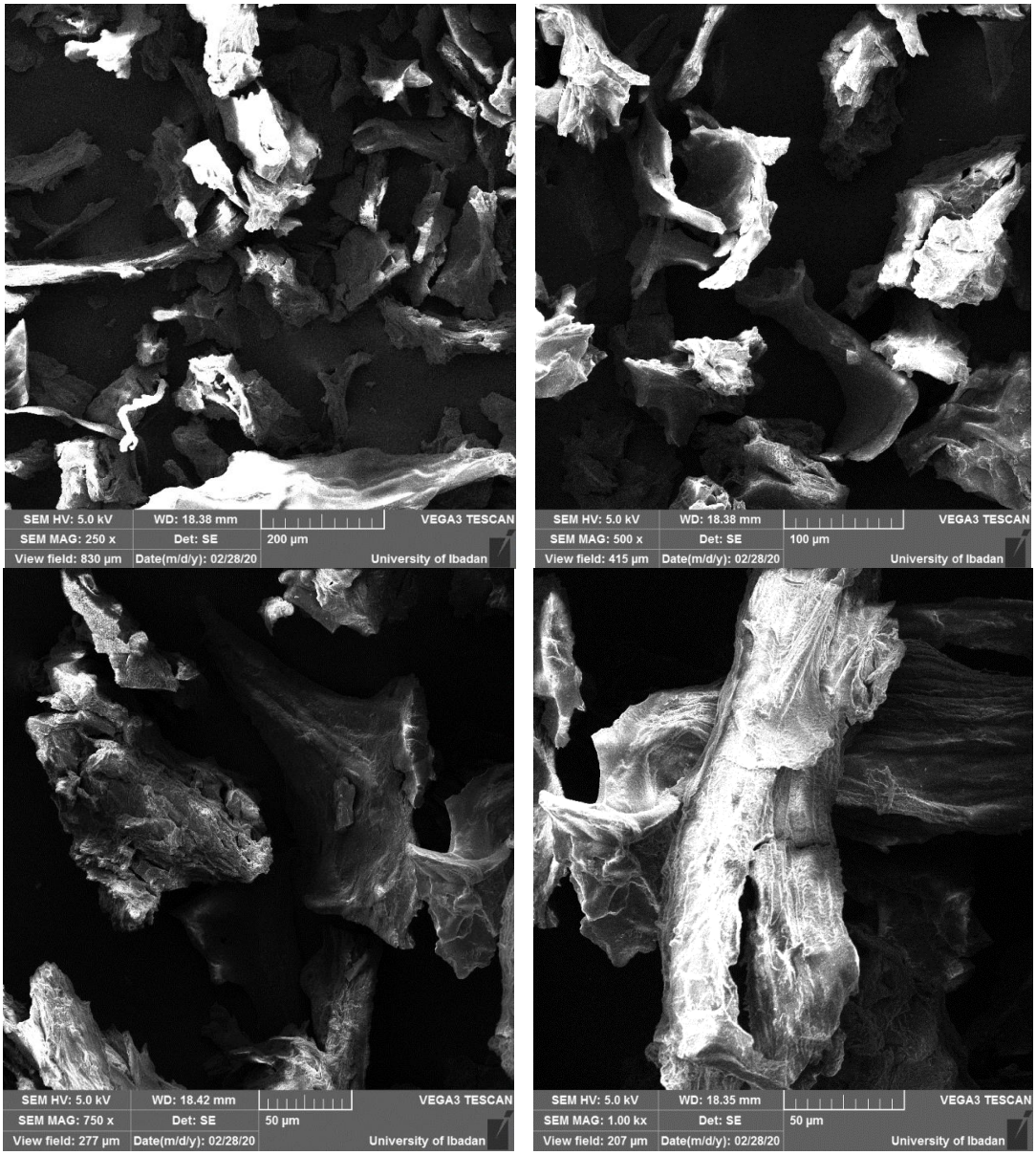
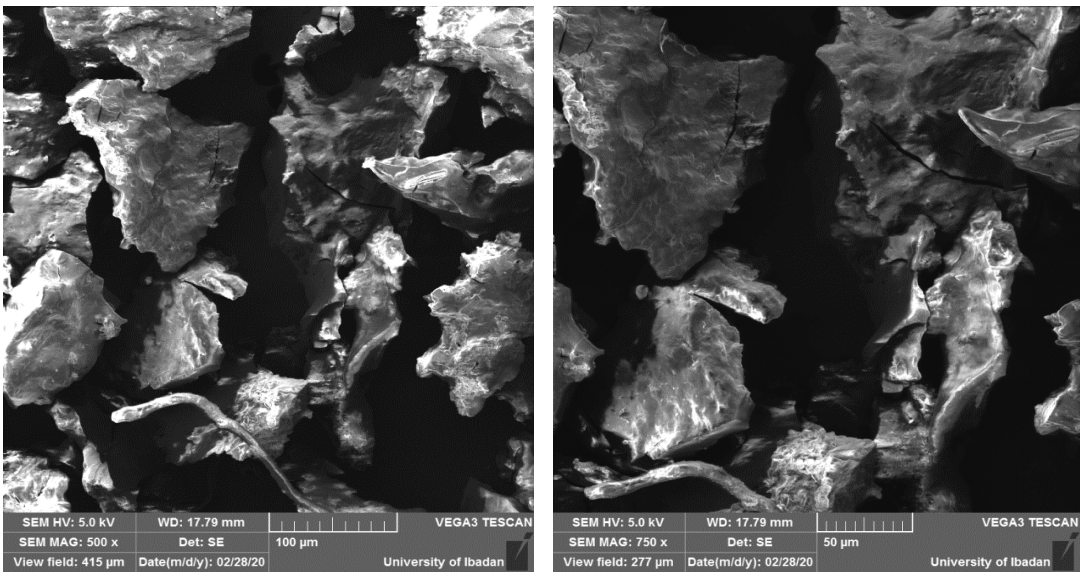


Figure 6: Scanning Electron Micrographs of Sample A1, A2, A3 and A4 (Cellulose microparticles of Sugarcane Bagasse obtained using 60 % and 65 % Sulphuric acid for 45 minutes).



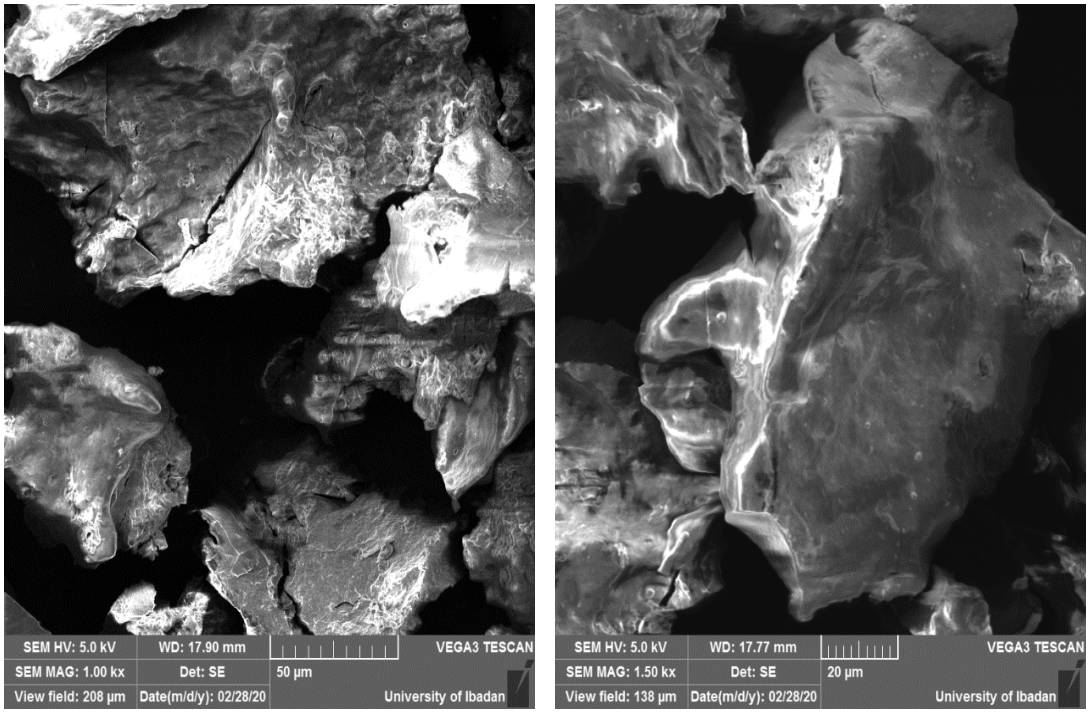


Figure 7: Scanning Electron Micrographs of samples B1, B2, B3, and B4 (Cellulose microparticles of Corn cob obtained using 60 % and 65 % Sulphuric acid for 45 minutes) at varied magnifications.

DISCUSSION

The yields of cellulose from corn cob and sugarcane bagasse were 41.1% $^{w}/_{w}$ and 43.24% $^{w}/_{w}$ respectively. These yields were high enough for the study and for use in drug delivery systems.[21] [23],

The cellulose powder of corncob was observed to be cream in colour while that of sugarcane bagasse was off-white. The moderately fine cellulose powders were odourless and had irregular shapes as seen in the photomicrographs in Figures 1 and 2. The cellulose powders had rough surfaces which can be attributed to the amorphous regions thus making them suitable for inter-particle adherence and improvement of drug solubility.[27]

The cellulose powders were of neutral pH, however, the corn cob cellulose had a higher moisture content than the cellulose obtained from sugarcane bagasse (Table IV). The presence of moisture in a powder sample influences its chemical stability, crystal structure, flow properties, and compaction. It may also serve as a medium for microbial growth. Hence, cellulose obtained from corn cob may need to undergo appropriate drying before being used in drug formulations.

The Swelling Index of a powder describes its water or moisture-absorbing capacity. It is defined as the increase in the weight or volume of a powder when allowed to swell freely in water.[28] The swelling index is a significant pointer to the disintegration property of any powder as swelling is a mechanism for disintegration.[29] From Table IV, it was observed that the swelling capacity of the cellulose from corn cob was greater than that from sugarcane bagasse but the difference was not significant. This suggests that both corn cob and sugar cane bagasse are suitable disintegrant materials in tablet formulations.

The Bulk density of the powder, which is the mass-to-volume ratio of an untapped powder (including all the interparticulate void volume), is not an intrinsic property of a powder as it can vary from time to time based on the powder handling, the density and rearrangement of the powder particles. It is also dependent on the particle size distribution, shape, and the cohesive forces between the particles.[30];[31] The tapped density, however, is the density of the powder after compaction and can be obtained by mechanical tapping until no further change in volume is observed. It is affected by the particle shape, particle size, electrostatic forces between particles, and the pressure applied to ensure compaction.[30] The bulk and tapped densities are indicative of a powder's packing properties. From Table IV, it was observed that the tapped densities of both cellulose powders were higher than their corresponding bulk densities. The bulk and tapped densities of corn cob cellulose were however higher than (almost twice) that of sugarcane bagasse. This implies that the cellulose from corn cob had a larger volume reduction with reduced porosities and the particles are more densely packed.[31] The difference observed could also be attributed to the differences in the particle shapes and size distribution which influence the arrangement and packing character of the particles.

The Particle density is a measure of the compaction characteristics of a powder and is the density of the

powder excluding voids and interparticle pores.[31] Dense powders may require a higher compression pressure to achieve cohesive but less friable products with good mechanical strength.[32] From Table IV, it was observed that corn cob cellulose had a higher particle density than that obtained from sugarcane bagasse.

The Flow properties of the cellulose powders were determined using Hausner's Ratio, Carr's Index, Flow rates, and Angle of Repose. The Hausner's Ratio and Carr's Index were calculated from the bulk and tapped densities.

Hausner's ratio, defined as the ratio of tapped to aerated bulk densities, is indicative of the degree of densification that would occur during a tableting process. High values predict significant densification of powders while low values predict better flowability. A Hausner's ratio of <1.25 implies good flowability. The cellulose powders from corn cob and sugarcane bagasse had good flowability as observed from Table IV.

Carr's index measures a powder's flowability and compressibility properties and is an indirect pointer to a powder's fluidity. A low value is suggestive of better flowability but a poorer compressibility while a high value signifies poor flowability but better compressibility. Carr's indices below 15 represent good flow properties (Ayorinde *et al.*, 2016). The cellulose powders can be said to have good flow properties, with the sugar cane bagasse cellulose having higher and lower values ($p < 0.05$) for flow rate and angle of repose respectively (Table IV).

The Angle of Repose, an angle to the horizontal plane to which the powder can be piled without slumping, is characteristic of the internal friction or cohesion of the particles. It is predictive of the flow properties of a powder and is dependent on the particle size distribution, morphology, and the frictional forces between the powder particles. Values are high if the powder is cohesive and low if the powder is non-cohesive. A high value is indicative of a decreased particle size and vice versa. A powder with an angle of repose <30° is a free-flowing powder while that with an angle of repose >40° is a poorly-flowing powder. (Ayorinde *et al.*, 2016) The cellulose obtained from sugarcane bagasse can be said to be more free-flowing with a significantly lower value of the angle of repose. The sugar cane bagasse cellulose probably possesses non-cohesive forces between the particles and better flow properties while cellulose obtained from corn cob can be said to have a fair flow with cohesive forces between the particles.

Viscosity is a measure of resistance to flow or deformation by shear or tensile stress. High viscosity values indicate high resistance to flow due to high internal friction and vice versa.[27] The viscosity value for the cellulose obtained from sugarcane bagasse was three times that of corn cob cellulose at a spindle size of 3 and speed of 20 rpm. However, as the speed increased from 50 to 100 rpm, the cellulose powders had higher viscosities. Generally, at constant spindle size, the viscosity of both cellulose powders increased with an increase in speed.

The cellulose powders showed absorbance spectra regions that were similar but with varied intensities. Both cellulose samples presented a wide band between 3200 and 3500cm^{-1} that specifies the free O-H stretching vibration of the O-H in cellulose molecules. The spectra of both samples showed characteristic C-H vibration at 2924.25 cm-1. The vibrational peak detected at 1385cm^{-1} is related to the bending vibrations of the C-H and C-O bonds in the polysaccharide aromatic rings. A peak at 900 cm^{-1} associated with the glycosidic linkages between glucose units in cellulose was observed in the spectrum of Sugarcane bagasse.

The peaks observed at 1641.66 and 1646.36cm^{-1} are due to the C-O stretching vibrations of the acetyl and uronic ester groups from pectin, hemicellulose, or the ester linkage of the carboxylic group of ferulic and p-coumaric acids of lignin or hemicellulose.[6] These peaks may also be due to the O-H bending of the adsorbed water.

The end product of the cellulose extraction processes still contain hemicellulose and lignin components which implies that these impurities have not been completely removed.

Cellulose materials are expected to be white in colour, after acid hydrolysis; however, the cellulose obtained had a black colouration, probably due to the presence of lignin in the cellulose powders of sugarcane bagasse and corn cob used in their preparation. The cellulose sources (corn cob and sugarcane bagasse) can be said to have a very high lignin content which probably was not completely removed by the acid hydrolysis; this could be responsible for the black colour obtained. Production, quality, and dimensions of nanoparticles have been found to be influenced by the pre-treatment methods and the hydrolytic conditions such as the reaction time, acid concentration, and purity.[33],[5] However, hydrolysis of cellulose with sulphuric acid to produce crystalline cellulose material is effective as it gave good yields as observed from Table I.

Materials of samples A3, A4, B3, and B4 which were hydrolysed with 65 % $^{v}/_{v}$ sulphuric acid were closely packed and did not separate into single crystals as seen in Figures 6 and 7 Whereas, hydrolysing the cellulose powders of both corn cob and sugarcane bagasse with 60 % $^{v}/_{v}$ sulphuric acid as observed in samples A1, A2, B1, and B2 gave single and well-defined microparticles upon drying. Hence, a low or optimum acid concentration may be required to produce particles that are non-clustering.

1. The surface morphology of the hydrolysed micro-particles as determined by scanning electron microscope

(SEM) is shown in Figures 6 and 7; they were amorphous in nature and had rough surfaces with pits. The shape of sugarcane bagasse cellulose micro-particles was rectangular while that of corncob was ellipsoidal. The presence of the pits observed indicates increased surface area and this could make reactive and suitable for adsorption and functionalization reactions.

The FT-IR spectra showed that the hydrolyzed cellulose microparticles have hydroxyl groups in addition to their high surface-to-volume ratio which makes them suitable for the introduction of any chemical functionality on their surface and modifying the type of interactions they undergo. This is advantageous in that, the cellulose microparticles can be employed in the formulation of water-soluble, ionizable drugs. Their surfaces can also be chemically altered or modified in fabricating carriers that modulate the loading and release of drugs that do not normally bind to cellulose such as hydrophobic and non-ionizable drugs.[5]

CONCLUSION

High yield of cellulose materials, possessing good physicochemical properties were extracted from two agricultural wastes, corn cob and sugar cane bagasse. Hydrolysis of the extracted cellulose produced microparticles with amorphous characteristics and potential for use in drug delivery.

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