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Isolation and Characterization of Cellulose from Underexploited Golden Melon Skin

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Abstract

Golden melon skin (GM) is an underexploited plant resource in Nigeria from which cellulose (GMC) was isolated and characterized. Characterization was achieved using Fourier transform-infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis, and scanning electron microscopy. GMC was further evaluated for its water holding capacity (WC), oil holding capacity (OC), water swelling capacity (SC), and heavy metal adsorption capacity. FT-IR spectroscopy revealed peaks corresponding to GMC, while the XRD diffraction planes exhibited by GMC were typical of cellulose I crystals with a crystallinity index of 40%. The thermal degradation of GMC revealed a first mass loss at 190–295 °C, second loss at 305–410 °C, and third loss 285–430 °C. The WC was 11.62 g/g, OC was 2.75 mL/g, and SC was 9.32 mL/g. The heavy metal adsorption capacity of GMC toward Cu (II) was 34.52 mg/g, and it was 28.73 mg/g toward Pb (II) in an aqueous solution. These results show that GM is a potential source of cellulose, which might have useful applications.

Abstrak

Isolasi dan Karakterisasi Selulosa dari Kulit Melon Emas yang Belum Dimanfaatkan secara Maksimal. Kulit melon emas (*Golden melon skin* (*GM*)) adalah sumber kekayaan hayati di Nigeria yang belum dimanfaatkan secara maksimal, dimana selulosanya diisolasi (*Golden melon Cellulose* (*GMC*)) dan dikarakterisasi. Karakterisasi dilakukan dengan menggunakan spektroskopi *Fourier Transform-Infrared* (*FT-IR*), Difraksi sinar-X, analisis termogravimetri, dan *Scanning Electron Microscopy*. Selanjutnya, *GMC* dievaluasi terhadap sifat kapasitas tahan air (*water holding capacity* (*WC*)), kapasitas tahan minyak (*oil holding capacity (OC)*), kapasitas pengembangan oleh air (*water swelling capacity* (*SC*)), dan kapasitas penyerapan logam berat. Spektroskopi FT-IR menampakkan puncak yang berhubungan dengan *GMC*, sementara difraksi XRD dari *GMC* menampilkan kristal I selulosa dengan indeks kristal 40%. Degradasi termal dari *GMC* menunjukkan penurunan massa yang pertama pada suhu 190-295 °C, penurunan kedua pada 305-410 °C, dan yang ketiga pada 285-430 °C. *WC* yang didapat sebesar 11,62g/g, sedangkan *OC* dan *SC* masing-masing adalah 2,75 mL/g dan 9,32 mL/g. Kapasitas penyerapan logam berat *GMC* terhadap Cu(II) adalah 34,52 mg/g, sedangkan terhadap Pb(II) adalah 28,73 mg/g dalam larutan encer. Hasil ini menunjukkan bahwa *GM* merupakan sumber selulosa yang potensial, yang mungkin dapat digunakan pada berbagai aplikasi yang bermanfaat.

Keywords: cellulose; cucurbitaceae; golden melon; SEM; XRD

Introduction

Lignocellulosic biomass is an underutilized source of renewable feedstock with the principal renewable biopolymer forms being lignin, hemicellulose, and cellulose [1-3]. Among the different forms of known biopolymers, cellulose is of great importance with its major sources being wood and cotton. Over the years, there have been searches for alternative sources of cellulose as a renewable resource to produce biodegradable and biocompatible materials [4].

Due to its abundant availability, low weight, renewability, degradability, and low abrasive property [5,6], cellulose has applications in the textile, cosmetic, construction, paper, and food industries [7-9]. As a result of the different possible applications of cellulose, there is an increasing demand for its supply but the major conventional sources are insufficient to meet the demand. Thus, there is need to identify other non-conventional renewable sources to produced cellulose to meet this increasing demand.

Attention has drifted toward unexploited or underexploited renewable materials [10,11] to identify non-conventional sources of cellulose. Some of these unexploited and underexploited renewable materials include agricultural waste. Among such agricultural wastes is golden melon skin (GM). Golden melon (*Cucumis melo* family Cucurbitaceae) is a bright-yellow melon with a pale green to white inner flesh [12]. It is a drooping herbaceous plant with alternating deep green leaves of about 7–15 cm diameter on long petioles with shallow lobes and several spiky margins [13]. The fruit is edible, and the outer skin of the fruit is thrown away as waste when the fruit is eaten. GM is unexploited in Nigeria as it has no specific use. The present study focused on finding applications for this discarded unexploited GM by isolating cellulose from GM.

A few unconventional sources of cellulose have been identified; some of these sources are not sustainable while others serve other important purposes. To the best of our knowledge, no study has isolated cellulose from GM. As GM is presently waste in Nigeria, the concept of the present study was to convert this waste (GM) into a useful product. Therefore, the main objectives of this study was to isolate and characterize cellulose from GM.

Materials and Methods

Materials. Golden melon fruit was obtained from a local market in Belo Horizonte, Minas Gerais, Brazil. The fruit was later identified at the Department of Botany and Microbiology, University of Ibadan, Ibadan, Oyo state, Nigeria. Glacial acetic acid, sodium hydroxide, sodium chlorite, sulfuric acid, and all other chemicals used in this study were purchased from Sigma-Aldrich (Belo Horizonte, Brazil). The skin was separated from the fruit, air dried, and kept in a nylon bag before use.

Isolation of cellulose from GM. GM (150 g) was transferred to a 3 L beaker. An alkali solution (2 wt% NaOH) was added and heated at 80 °C for 5 h with continuous stirring using a Fisatom mechanical stirrer. The mixture was cooled, filtered, washed with deionized water several times until alkali free, and oven dried at 50 °C. The residue was bleached with a mixed solution made of equal volumes (1:1) of acetate buffer (27 g NaOH and 75 mL glacial acetic acid, diluted to 1 L of distilled water) and aqueous sodium chlorite (1.7 wt% $NaClO_2$ in deionized water) as described previously [14]. The mixture was stirred at 80 °C for another 5 h. The resulting fibers were washed repeatedly in deionized water until the pH of the fibers was neutral. The bleaching step was repeated twice until the fibers were completely white. The fibers were dried in an air-circulating oven at 50 °C for 24 h to produce cellulose with an estimated yield of about 23%.

Characterization. The functional groups in GMC were determined by Fourier transform-infrared (FT-IR) spectroscopy (Perkin Elmer, spectrum RXI 83303; Waltham, MA, USA). The GMC was blended with KBr, pressed into pellets, and analyzed in the range of 400–4,500 cm^{-1}. The X-ray diffraction (XRD) pattern was obtained using an X-ray diffractometer (XRD-7000X-Ray diffractometer, Shimadzu, Tokyo, Japan) with filtered Cu Kα radiation operated at 40 kV and 40 mA. The XRD pattern was recorded from 10 to 80 °C of 2θ/s with a scanning speed of 2.0000° of 2θ/min. Thermal stability and the fraction of GMC volatile components were monitored with a DTA-TG apparatus (Shimadzu, C30574600245) under a nitrogen atmosphere. Surface morphology was studied using FEI quanta 200 (model EDAX EDS; Hillsboro, OR, USA) operated using Genesis software, version 5.21. The powdered GMC was coated with gold using the sputtering technique to increase electrical conductivity and the quality of the micrographs.

Authentication of GMC. Isolation of cellulose was confirmed by comparing the FT-IR spectrum and XRD pattern of GMC with those of commercial cellulose (UFMG, Belo Horizonte, Brazil). The commercial cellulose was prepared from eucalyptus kraft wood pulp with high alpha-cellulose content (96–98%).

Water holding capacity. Water holding capacity (WC) was evaluated following the method described by Zhang et al. [15] Thus, 0.5 g (W_1) of GMC was dispersed in 10 mL distilled water in a pre-weighed, clean centrifuge tube (W), which was placed in a water bath at 37°C for 30 min. The tubes were centrifuged for 15 min at 4,000 rpm, the supernatant was removed, and the centrifuge tubes with distilled water-soaked GMC were weighed (W_2). WC was estimated as:

$$WC\ (g\,g^{-1}) = \frac{(W_2 - (W + W_1)}{W_1} \quad (1)$$

Oil holding capacity. Oil holding capacity (OC) was determined by weighing 0.2 g (W) of GMC into a calibrated centrifuge tube containing 5 mL (V_1) of *Picralima nitida* seed oil. The mixture was stirred for 10 min after which it was centrifuged for 30 min at 5,000 rpm. The supernatant oil (V_2) was gently removed, and

the absorbed oil was estimated as the difference between V_1 and V_2. OC was calculated as described by Lu et al. [16]:
Why is Picralima Nitida seed oil used?

$$OC\ (mLg^{-1}) = \frac{V_1 - V_2}{W} \quad (2)$$

Swelling capacity. Swelling capacity (SC) was determined by placing 0.5 g (W) of GMC in a calibrated tube, measuring its initial bed volume (V_1), mixing it with 10 mL of distilled water, followed by vigorous shaking. The tube with its content was placed in a water bath at 25 °C for 24 h, the final volume (V_2) was measured, and SC was calculated using Eq. 4 [17].

$$SC\ (mLg^{-1}) = \frac{V_2 - V_1}{W} \quad (3)$$

Heavy metal adsorption capacity. Lead nitrate ($Pb(NO_3)_2$) and copper sulfate ($Cu(SO_4)\cdot 5H_2O$) salts were used to prepare the salt solutions in de-ionized water. The metal adsorption study was carried out by separately shaking 0.1 g of GMC with a 50 mL solution (100 mg/L) of the metals in different beakers at 25 °C and 200 rpm for 3 h. This solution was later centrifuged for 10 min at 5,000 rpm, and the metal concentrations before and after adsorption were determined using an atomic absorption spectrometer (Varian AA240FS; Palo Alto, CA, USA). The Varian AA240FS was calibrated using a reference standard with a sensitivity of > 0.9 absorbance from 5 mg/L Cu, while the wavelength was maintained at a repeatability of ± 0.04 nm. The method was validated according to the method described by the European Union standards for foodstuff [18]. The parameters included selectivity, range of linearity, reproducibility, trueness according to a certified reference material, method detection limit, detection capacity, and quantification limit. The metal ions adsorption capacity of GMC was calculated using Eq. 4:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (4)$$

Where q_e is the adsorption capacity in mg/g, C_o and C_e are the initial and final concentrations (mg/L) of adsorbate (Pb and Cu) in solution, respectively, and V and M are the volume (L) of the metal ion solution and weight (g) of the GMC used, respectively.

Statistical analyses. All data are expressed as mean ± standard error of the mean. Analysis were carried out in triplicate (n = 3). A p-value < 0.05 was considered significant.

Results and Discussion

Characterization. The FT-IR results of the authentic commercial cellulose and GMC are presented in Figure 1. A band observed at 3,410 cm^{-1} in the GMC and commercial cellulose was assigned to O-H stretching frequency. The peak at 2,845 cm^{-1} was attributed to alkane groups. The spectra revealed bands at 1,106 and 1,025 cm^{-1} in GMC and the commercial cellulose, which represented the C-O vibrational stretching of cellulose and the C-O-C pyranose ring stretching vibration, respectively [19]. Signals found at 906 cm^{-1} in GMC and the commercial cellulose were assigned to stretching at β-(1→4) glycosidic linkages, whereas the peak at 1,361 cm^{-1} was characteristic vibrational stretching of C-O bonds in the polysaccharide rings. Label peaks.

The X-ray diffractograms of GMC and commercial cellulose are presented in Figure 2. Sharp peaks were shown by GMC and commercial cellulose at around 18° and 22.5° 2θ angles, which were considered diffraction planes of 110 and 002 [17,19]. The crystallinity index (I_c) was determined using the height of the 200 peak (I_{002}, 2θ = 22.5°) and the minimum intensity between the 200 and 110 peaks (I_{AM}, 2θ=18°) and was expressed as:

$$I_c(\%) = \frac{I_{002} - I_{AM}}{I_{002}} \times 100 \quad (5)$$

Where I_{002} represents both the crystalline and amorphous material, and I_{AM} represents the amorphous material. The diffraction planes obtained were typical of the cellulose I crystalline form. The crystallinity index of GMC was 40%.

Thermal degradation was studied using a thermogravimetric analysis (TGA), as shown in Figure 3. The initial loss in mass occurred at 50–110 °C, which was attributed to loss of water molecules in the GMC. Degradation of cellulose occurs mainly via dehydration, depolymerization, and glucosan formation [20-23]. GMC had its first mass loss at 190–295 °C, which was attributed to degradation leading to 1,4 and 1,6 anhydroglucopyranoside, while the second stage at 305–410 °C was depolymerization at the 1,4 glycosidic bonds. The third stage occurred at a higher temperature and included pyrolysis to lower molecular weight molecules. The surface morphology of GMC was evaluated by scanning electron microscopy (SEM). The image is shown in Figure 4. The surface of the GMC appeared compact but also exhibited a lumpish structure, which may have occurred because of the strong intramolecular hydrogen bonds that exist in the molecule. To include derivative weight in Thermogram.

WC, OC, SC, and metal adsorption capacity of the GMC. The WC, OC, and SC results are presented in Figure 5. WC was 11.62 ± 0.01 g/g, OC was 2.75 ± 0.01 mL/g, and SC was 9.32 ± 0.02 mL/g. The WC was

higher than the values reported for standard flour [24] and dietary fiber [25]. GMC held water better than oil. This may be due to the ability of the hydroxyl groups in GMC to form hydrogen bonds with water molecules. This ability to hold water is an indication that GMC may find applications in areas where water retention is required. The tendency of GMC to adsorb heavy metals (Pb and Cu ions) was evaluated, and the results are presented in Figure 6. These metals are toxic and capable of causing diseases in humans [26]. They have been found in water, food, and some domestic products [27]. The validation results show that the Varian AA240FS instrument was precise, accurate, and followed excellent linearity. The adsorption capacity of the GMC toward

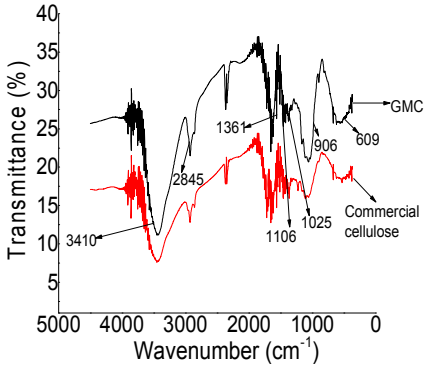

Figure 1. Fourier Transform-Infrared Spectra of Commercial Cellulose and Golden Melon Skin (GMC)

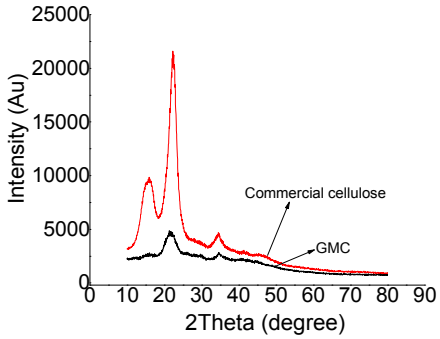

Figure 2. X-ray Diffraction Spectra of Commercial Cellulose and Golden Melon Skin (GMC)

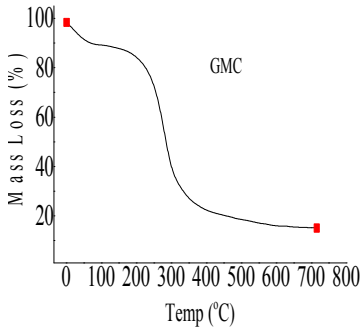

Figure 3. Thermogravimetric Analysis of Golden Melon Skin (GMC)

Cu (II) ions was 34.52 ± 0.01 mg/g and 28.73 ± 0.02 mg/g toward Pb (II) ions. These values are higher than those reported by Jiang et al. [28], Futalan et al. [29], and Putra et al. [30]. The tendency of GMC to adsorb these metals may be associated with the presence of hydroxyl functional groups; these hydroxyl groups have

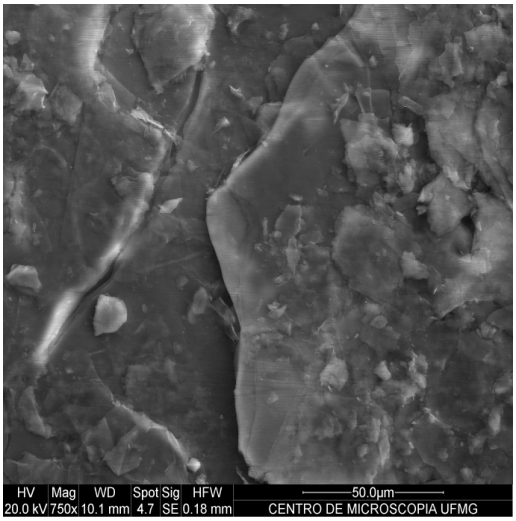

Figure 4. Scanning Electron Micrograph of Golden Melon Skin

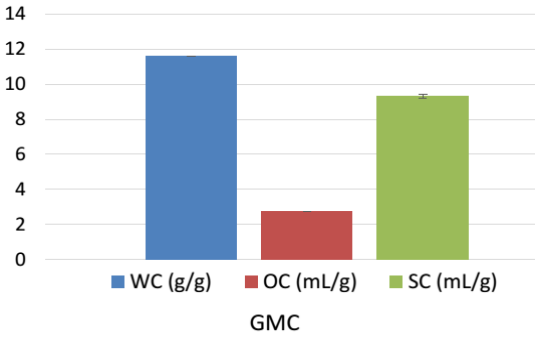

Figure 5. Water Holding Capacity (WC), Oil Holding Capacity (OC), and Swelling Capacity (SC) of Golden Melon Skin (GMC)

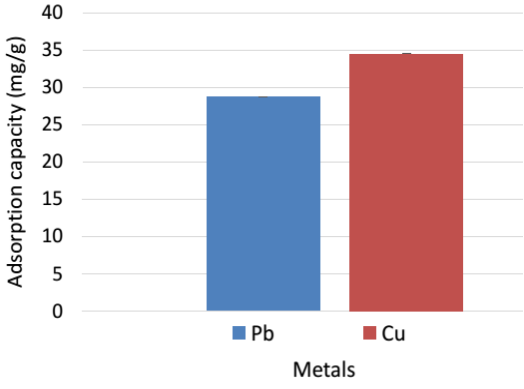

Figure 6. Adsorption Capacity of Golden Melon Skin (GMC) Toward Pb^{2+} and Cu^{2+} Ions

the capacity to exchange their hydrogen atoms for metal ions via an ion-exchange mechanism or they also form a complex with these metal ions. It may be that both ion exchange and complexation were occurring at the same time on the GMC surface.

Conclusion

This study focused on isolating cellulose from GM as an alternative source of cellulose. GMC was characterized using FT-IR spectroscopy, XRD, TGA, and SEM. GMC was further analyzed for WC, OC, SC, and metal adsorption capacity. The results revealed that GMC exhibited properties typical of the cellulose I crystalline form. The WC, OC, SC, and adsorption capacities toward Cu (II) and Pb (II) in aqueous solution showed that the GM is a potential source of cellulose with useful applications.

Acknowledgments

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