EXTRACTION AND CHARACTERIZATION OF CELLULOSE FROM AGRICULTURAL WASTE ARGAN PRESS CAKE

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Argan press cake (APC) is a low-cost agricultural waste material generated from the oil production of argan nuts. It is a dark-brown powder containing cellulose and other components, such as hemicelluloses, proteins, and lipids. In this study, an alkaline processing approach consisting of applying a mild cooking treatment at 80 °C in a solution containing sodium hydroxide (12%) and sodium sulfate (8%) was developed to extract cellulose from APC. Yellowish cellulose pulp was thereof obtained and was further subjected to an $H_0PH_1E_p$ bleaching operation to enhance the purity of cellulose to a large extent. Sugar analysis, molecular weight analysis and other spectroscopic techniques demonstrated that the extracted cellulose could be classified as cellulose powder that would be qualified for pharmaceutical and food applications.

Keywords: argan press cake, cellulose, extraction, molecular weight, sugar analysis

INTRODUCTION

The argan tree is a tropical plant that grows only in the semi-desert region of the south-western region of Morocco. It belongs to the *Sapotaceae* family and represents the only endemic species of the genus *Argania*.[1] In spite of its 'forest' status, the argan tree is indeed a multipurpose tree, mainly used for fodder and as an oil-yielding resource.[2] The fruit of the argan tree is (similar to walnut tree or almond tree) a stone-fruit with pulp covering a lignified endocarp (the nut) containing one to three kernels (the seeds), from which an edible oil can be extracted by various methods,[3-5] such as hand compression,[6] mechanical press technique, and solvent extraction. The most effective process for collecting argan oil is the mechanical press method, where the ripe-fruit pulp and peel are removed, and then argan nuts go through consecutive drying and grinding stages to produce a brownish dough. The dough is pressed directly to produce oil with approximately 43% yield. The extraction residue, known as argan press-cake (APC), is a dark-brown powder and generally still contains approximately 10% of oily components.[7] APC is considered as a waste agricultural material and is currently used for cattle feed. Previous studies documented its composition of 26.3% moisture, 3.6% ash, 24.6% nitrogen-containing derivatives, 18.9% lipids, and 26.6% of carbohydrates with 17.6% cellulosic products.[8-9]

Cellulose is one of the main components of APC, which makes it potentially attractive and a low-cost source of cellulose. It has been well known that cellulose carries various interesting properties, which can lead to diverse applications in paints, personal products,[10,11] tableting aid for pharmaceuticals, and stabilizers or fat replacement for foods.[12,13] In addition, cellulose can also produce considerable derivatives by means of chemical and physical modifications. One of the most valuable cellulosic derivatives is microcrystalline cellulose (MCC), which is generated by acid or enzymatic hydrolysis of cellulose with high cellulose I content.[14] Acid

penetrates the amorphous region and cleaves the β-1,4-linkage between cellulose repeating units to produce cellulosic products of low molecular weight containing most oligosaccharides and a small amount of water-soluble glucose. As the original source of MCC production, the cost of cellulose production associated with the production of MCC and other value-added derivatives needs to be considered. In this study, our aim is to develop a facile and effective extraction to obtain relatively low-cost cellulose with high purity from agricultural waste APC. The physicochemical properties of the extracted cellulosic product were thoroughly investigated.

EXPERIMENTAL

Materials

All reagents were purchased from Aldrich Chemical Company and used as received, unless otherwise specified. Kraft pulping was performed using a high Parr Reactor model: Buchiglasuster, BMD 300 (Switzerland). Argan press cake was obtained from Morocco (Tugaza Argan, Morocco).

Extraction and purification of cellulose from argan press cake

Removal of lipids from argan press cake

Lipids present in APC were removed using the Soxhlet extraction method. The composition of lipids in argan oil has been well studied and documented by the capillary gas chromatography analysis in the literature.[7-8] APC (100 g) was added in a round bottom flask of 1 L filled with 500 mL of toluene. The removal of lipids from APC was performed for 3 h. Toluene solvent containing lipids was collected under reduced pressure and then was subjected to rotary evaporation to remove approximately 3.8 g of lipids from APC. The rest of the material was pale yellow, denoted as crude APC, and was ready for the next extraction of cellulose.

Extraction of cellulose from argan press cake (Kraft pulping)

Kraft pulping was conducted to extract crude cellulose from APC in a round bottom flask of 1 L filled with an aqueous solution of NaOH (12 wt%) and Na_2SO_4 (8 wt%). The temperature was raised to 80 °C and maintained for 90 min. At the end of the reaction, the resulting cellulose pulp was filtrated, rinsed with fresh water to remove alkali, air dried, and stored in plastic bags for further purification.

Other extraction approaches were carried out in this study to evaluate the effectiveness of Kraft pulping. In the first extraction, the APC free of lipids at 1% by weight was soaked in a successive treatment with deionized (DI) water at 90 °C for 6 h and then with ethanol at 45 °C for 2 h. The last APC suspension was filtered, rinsed with DI water and air dried. The sample was labeled as APC-WE. In the second extraction approach, acid pulping was used,[15] in this process APC at 5 wt% was soaked in an aqueous solution of H2SO4 (0.75 wt%) at 75 °C for 1 h. Then, it was washed with plenty of water and neutralized with diluted NaOH. The sample obtained was labeled as APC-AC.

Purification of crude cellulose (cellulose bleaching)

The purification of crude cellulose obtained from APC Kraft pulping was performed using a bleaching sequence operation containing H_0-stage, P-stage, H_1-stage and E_p-stage in the order $H_0PH_1E_p$, as described below. It should be noted that hypochlorite as a reagent is now being phased out of commercial pulp bleaching due to the serious environmental effect because of releasing organic chlorine substances and volatile chloroform. Therefore, nowadays, most bleaching plants have replaced hypochlorite with chlorine dioxide, following the alkaline extraction. In this study, we performed a pilot experiment using hydrocholorite rather than chlorine dioxide in order to seek the feasibility of bleaching APC and obtaining a high quality cellulose product. The bleaching operation of APC with chlorine dioxide instead of hypochlorite would be our next objective, which would possibly involve collaboration with industry.

H-stage: crude cellulose of 100 g was added to a plastic bag containing 900 mL of 1 wt% NaOCl (w:w of crude cellulose weight), solution pH was about 12.55. The plastic bag was placed in a water bath at 45 °C for 1 h. At the end of the reaction, the sample in the plastic bag was washed with fresh water until NaOCl was completely removed and the sample was ready for use in the next step.

P-stage: a solution mixture of 900 mL consisting of 2 wt% H_2O_2 (w:w of crude cellulose weight), 0.5 wt% $MgSO_4.7H_2O$ (w:w of crude cellulose weight), and 3 wt% NaOH (w:w of crude cellulose weight) was added to the plastic bag that already contained the cellulose pulp obtained from the first H-stage, the solution pH was about 12.8. The plastic bag was then placed in the water bath and the reaction was performed at 60 °C for 1 h. Subsequently, the cellulose pulp in the plastic bag was washed to remove chemicals and was ready for use in the next step.

Ep-stage: after repeating the H-stage as shown above, the last bleaching step was performed in the same plastic bag containing the cellulose pulp obtained from the second P-stage, where a 900 mL fresh solution consisting of 1 wt% NaOH (w:w of crude cellulose weight) and 0.5 wt% H_2O_2 (w:w of crude cellulose weight) was added to the plastic bag; the solution pH was about 12.2. The reaction was conducted in a water bath at 70 °C for 90 min. At the end, the cellulose pulp was washed thoroughly to remove chemicals and then dried in the oven at 60 °C. The resulting cellulose was weighed and the yield of

the purified cellulose was determined. The sample obtained was labeled as APC-cell.

Material characterization of APC-cell

The Infrared (IR) spectra of APC-cell were recorded using a Fourier Transform IR 400 Spectrometer (FTIR) (Perkin Elmer, USA), equipped with Universal Attenuated Total Reflectance (UATR). The following parameters were used: resolution 4 cm^{-1}, spectral range 650-4000 cm^{-1}, number of co-added scans 32.

Scanning Electron Microscopy (SEM) was performed using TM-1000 (Hitachi, Pleasanton, CA). A small amount of APC-cell powder was mounted on the SEM sample stage with a conductive carbon tape attached and the surface morphology of APC-cell was observed.

Thermal analysis of APC-cell was performed using Pyris1TGA (PerkinElmer, USA). Thermograms of the samples were recorded between 37 and 600 ºC at a heating rate of 10 ºC/min in a flow of N_2 at 20 mL/min. The Pyris Analysis software was used to calculate the first derivative of thermograms (DTG), as well as to estimate the percent weight loss and the decomposition temperature for each sample.

Wide angle X-ray diffraction (XRD) patterns were acquired using a SmartLab X-Ray Diffractometer (Rigaku HD 2711N, Japan). SmartLab uses a Cu target (λ = 1.541867 Å), voltage of 40 kV, and current of 44 mA. X-ray scans over the two theta scanning range of 5°-50° were performed to determine the crystalline morphology of the samples.

Sugar analysis

The purity of APC-cell was determined based on the monomer content measured after acid hydrolysis.[16] APC-cell of 300 mg obtained from the $H_0PH_1E_p$ bleaching sequence was added to 3 mL of 72% H_2SO_4. The mixture was heated at 37 °C for 60 min and then was diluted to 4% H_2SO_4 with deionized (DI) water, followed by an autoclave operation at 121 °C for 1 h. Next, the resulting solution was filtered (Grade 4 filter paper, Whatman, USA) and the filtrate was analyzed by normal phase High Performance Liquid Chromatrography (HPLC, Merck Hitachi) equipped with a refractive index detector and an Aminex HPX-87H column (Bio-Rad Labs, Hercules, CA). The HPLC running parameters were set at 45 °C with an aqueous solution of 5 mol/L H_2SO_4 as a mobile phase at a flow rate of 0.6 mL/min.

Dissolution of APC-cell for molecular weight (MW) analysis

APC-cell was dissolved in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solvent system to determine the molecular weight of APC-cell.[17] The APC-cell sample (4 mg) was suspended in 10 mL DI water at the room temperature, followed by two consecutive exchanges with 10 mL methanol in a time interval of 1 h each, and the sample solvent was then replaced by another two consecutive exchanges with 10 mL anhydrous DMAc. The first DMAc exchange lasted for 1 h and the second lasted overnight. At the end of each exchange, the solvent was removed from the sample suspension by vacuum filtration. After the last DMAc exchange, the activated APC-cell sample was transferred to a vial filled with 4.0 mL of 8% LiCl/DMAc (w:v) solvent. The mixture was stirred until a clear solution was achieved in about 2 h. The clear solution was diluted with 60 mL anhydrous DMAc to produce a solution of APC-cell with 1.0 mg/mL concentration for MW analysis. Next, Gel Permeation Chromatography (GPC, DAWN® HELEOS® II and the Refractive Index detector Optilab® T-REX, Wyatt Technology, USA), combined with High-Performance Liquid Chromatography (HPLC, 1260 Infinityl, Agilent, USA), was used to determine the MW of APC-cell. Data acquisition was carried out in 0.5 s intervals with ASTRA 6.1 software (Wyatt Technologies, USA). The mobile phase of 0.5% LiCl/DMAc (w:v) and the APC-cell sample solution were filtered through 0.25 µm filters (Millex LCR, Millipore, USA) prior to use. The system equipped with three separate columns (MIXED-B, 300 x 7.5 mm, Agilent, USA) was operated at 25 °C with a flow rate of 1 mL/min and the running time was 40 min. The calibration was done with polystyrene 30,000 g/mol at 0.5016 g/mL in 0.5% LiCl/DMAc.

RESULTS AND DISCUSSION

Extraction and characterization of cellulose from APC

Three different extraction methods were compared in this study. Figure 1 shows the FTIR spectra of the original APC free of lipids and the APC-WE extracted product from the water/ethanol treatment. Both spectra are overall similar, but there are some differences in the intensities of the vibrations 2916, 2850, (CH_2 stretching) and 1744 cm^{-1} (C=O stretching). This suggests that the APC still contains residues of organic acids.[18] However, the intensities of these peaks decrease in the APC-WE spectrum, as compared to that of APC, indicating that the water/ethanol treatment could continue to remove lipids from APC, whereas it may not be working well on the extraction of cellulose. In addition, the peak intensities of the vibrations 1031 and 1628 cm^{-1} significantly increase for APC-WE, which suggests that cellulosic and protein components have been concentrated as well after the water/ethanol treatment, although the yield of cellulose extraction is low.

Figure 2 shows the FTIR spectra of the APC and APC-AC obtained by acid pulping. The

spectrum of APC-AC shows a vibration at 1744 cm^{-1} associated with the presence of lipids, suggesting that the acid pulping removed a certain amount of oily chemicals from APC, exhibiting a similar effect to the water/ethanol treatment. However, a significant decrease in the intensity of the vibration at 1628 cm^{-1} is noted (due to the presence of proteins) in the spectrum of APC-AC. This indicates that acid pulping is a relatively efficient approach to remove protein components from APC. When comparing APC and APC-WE, a small amount of impurities, such as lipids and proteins, is still present, which demonstrates that acid pulping may not be efficient in the extraction of cellulose from APC.

Kraft pulping is a pre-extraction step to extract cellulose from APC prior to the $H_0PH_1E_p$ bleaching sequence. The yield of cellulose obtained from the Kraft pulping was of about 14.2%. Rather than more than 40% of cellulosic content in wood fiber, APC only contains the pure cellulose content (powdered form) excluding hemicellulose and lignin not beyond 20%,[8,9] and thereof obtaining 14% of pure cellulose from APC is actually considered a great accomplishment. From Kraft pulping, the resulting cellulosic product still had a light brownish color, which may indicate the presence of colored impurities. The $H_0PH_1E_p$ bleaching treatment was subsequently applied to further enhance the purity of cellulose. The FTIR spectra of APC and APC-cell after $H_0PH_1E_p$ bleaching are shown in Figure 3. The spectrum of APC-cell shows that impurities, such as proteins and lipids, were removed because the peaks at 1744 and 1628 cm^{-1} are greatly decreased or completely disappear. The typical peaks at 1033 and 1056 cm^{-1} are associated with the cellulosic macromolecule, indicating the enhanced presence of sugar components.

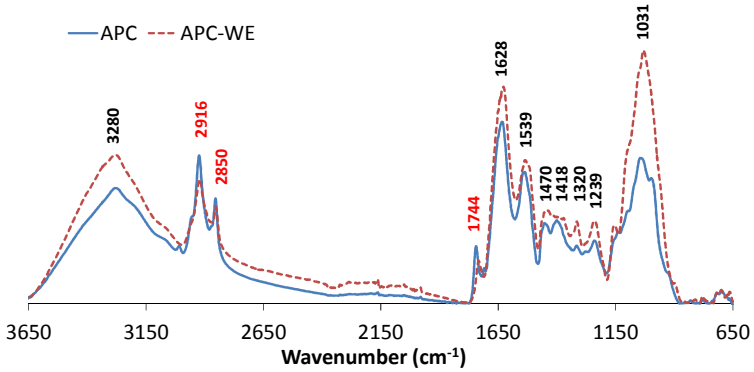

Figure 1: FTIR spectra of APC and cellulose extracted from APC by water/ethanol treatment (APC-WE)

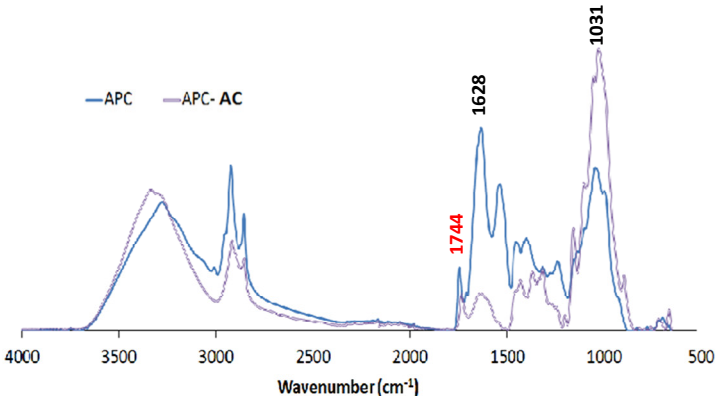

Figure 2: FTIR spectra of APC and cellulose extracted from APC by acid pulping (APC-AC)

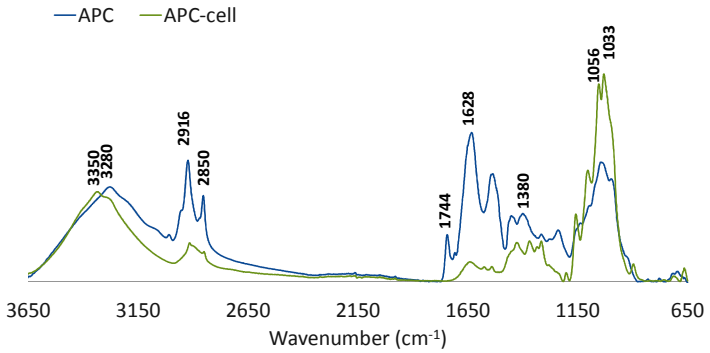

Figure 3: FTIR spectra of APC and cellulose extracted from APC by $H_0PH_1E_p$ bleaching sequence (APC-cell)

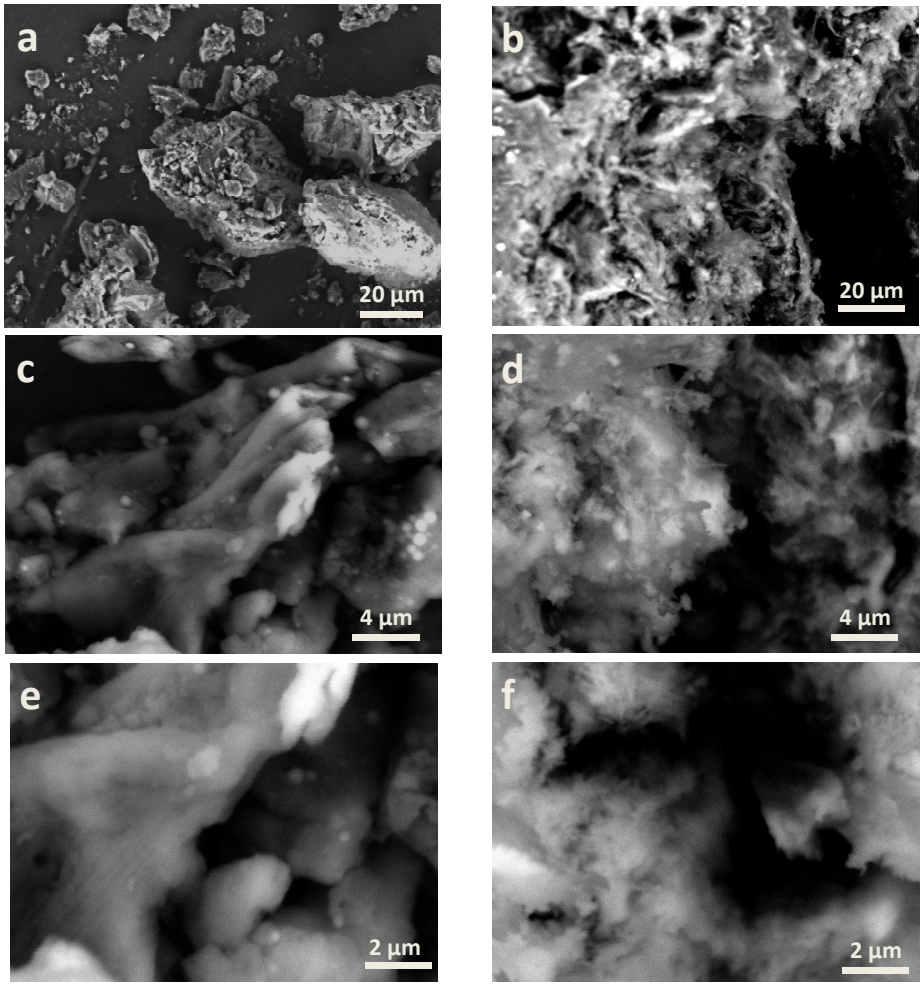

Figure 4: SEM images of APC (a, c, e) and cellulose extracted from $H_0PH_1E_p$ bleaching sequence (APC-cell) (b, d, f) under different magnifications

The results from the comparison amongst the FTIR spectra of the APC, APC-WE, APC-AC and APC-SC reveal that $H_0PH_1E_p$ combined with Kraft pulping is an effective extraction approach not only to enhance the purify of cellulose, but also to remove most impurities completely, as

compared to the water/ethanol treatment and acid pulping. The $H_0PH_1E_p$ bleaching sequence, containing a series of bleaching operations with hypochlorite (NaOCl), hydrogen peroxide (H_2O_2) in basic medium, followed by extraction with sodium hydroxide (NaOH) in the presence of a low concentration of hydrogen peroxide,[19,20] demonstrates the merit of producing cellulose from APC. Figure 4 shows the SEM images of APC and cellulose powder of APC-cell. At low magnification, as shown in Figure 4c-d, the surface of APC appears to be smoother than that of APC-cell, probably due to the presence of lipids in APC. Some small and white particulates aggregate easily, as observed in the APC image. This is not the case in APC-cell, which may provide evidence that the removal of impurities from APC has been successfully achieved. Fiber-like objects can be clearly identified in Fig. 4d and 4f, suggesting that cellulosic products have been well purified from APC. These SEM images further demonstrate the effectiveness of the removal of the impurities, which allows obtaining pure cellulose from APC via Kraft pulping and $H_0PH_1E_p$ bleaching operations.

Thermogram curves of APC and APC-cell are shown in Figure 5a-b and the maximum decomposition temperatures are shown in Table 1. The first derivative curve of weight loss of APC indicates that there are four decomposition stages in the APC, corresponding to the presence of four major components. According to FTIR analyses and the reference,[21] the first stage occurs at a maximum decomposition temperature of 54.5 °C in the range of 40-150 °C and is associated with absorbed water that accounts for approximately 9.3%. The second stage in the range of 150-300 °C shows the maximum decomposition temperature at 238.2 °C, suggesting that protein and lipid components may have been decomposed in this range. Protein and lipids may account for about 18% of the APC weight. The third stage in the range of 300-380 °C shows the maximum decomposition temperature at 333.1 °C, which is related to the cellulosic component[20] accounting for about 29% of the APC weight. The maximum decomposition temperature in the fourth stage in the range of 380-550 °C slightly shifts to 379.3 °C, perhaps due to the presence of impurities in APC. The component decomposed in the fourth stage could be lignin, which accounts for about 21.7% of the APC weight.[22] Given that the impurities have been removed in the case of APC-cell, the maximum decomposition temperature at 319.2 °C for APC-cell is similar to the decomposition temperature of pure cellulose. The decomposition rate of APC-cell in the range of 250-380 °C has greatly increased, as compared to that of APC, suggesting that the cellulosic component has been well purified and the weight loss of APC-cell associated with the cellulosic content is increased to about 48%. The cellulose and lignin contents in other types of biomass wastes account for about 60-70% and 8-35%, respectively.[23] For example, corn stalk contains approximately 62% cellulose (cellulose and hemicellulose) and 16% lignin, bagasse contains approximately 66% cellulose and 18% lignin, and rice straw contains approximately 61% cellulose and 24% lignin.[23] As compared with other agricultural biomass wastes, APC shows a relatively lower cellulose content, but an extra amount of lipid and proteins instead. Likewise, these lipid and protein ingredients show potential for food, nutrition and cosmetic applications.[24] The X-ray diffraction patterns of APC and APC-cell are shown in Figure 6, where APC-cell clearly shows three peaks at approximately 15°, 18.5° and 22.8°, corresponding to planes associated with Miller indices $1\bar{1}0$, 110, and 200, respectively. The crystallinity of APC-cell is estimated according to the peak profiling result treated by PeakFit software (http://www.sigmaplot.co.uk/) and calculated in terms of the ratio of sum of all peak area versus the sum of peak area at crystalline peak.[25] XRD results suggest that the cellulose extracted from APC via Kraft pulping and $H_0PH_1E_p$ bleaching operations (APC-cell) exhibits crystalline morphology of cellulose I with an enhanced crystallinity from 53.1% for unbleached APC to 66.2%.[26] This crystallinity of APC after the pulping treatment shows a value similar to other

agricultural biomass wastes, such as rice straw (64.3%)[27] and bagasse (61.6%).[28]

Sugar analysis of APC-cell

Crude APC and cellulose extracted from APC using the $H_0PH_1E_p$ bleaching sequence (APC-cell) were subjected to sugar analysis to compare the purity of cellulose. Figure 7a shows the chromatogram of APC, exhibiting high content of hemicelluloses (glucose, fructose, arabinose, galactose, xylose, and mannose).

The chromatogram of APC-cell reveals that the hydrolysis products were composed of almost pure glucose monomer, although other sugars, such as D-xylose and D-fructose, exist in a fairly small amount, less than 3% of the total sugars (Fig. 7b). The sugar analysis suggests that 95% purity cellulose has been achieved by extraction from APC via $H_0PH_1E_p$ bleaching.

Table 1
Decomposition temperatures (T*m*) of different components of APC and APC-cell

Sample IDs	Tm_1 (°C)	Tm_2 (°C)	Tm_3 (°C)	Tm_4 (°C)	Tm_5 (°C)
APC	54.5	238.2	333.1	379.3	N/A
APC-cell	N/A	N/A	330.8	378.4	449.2

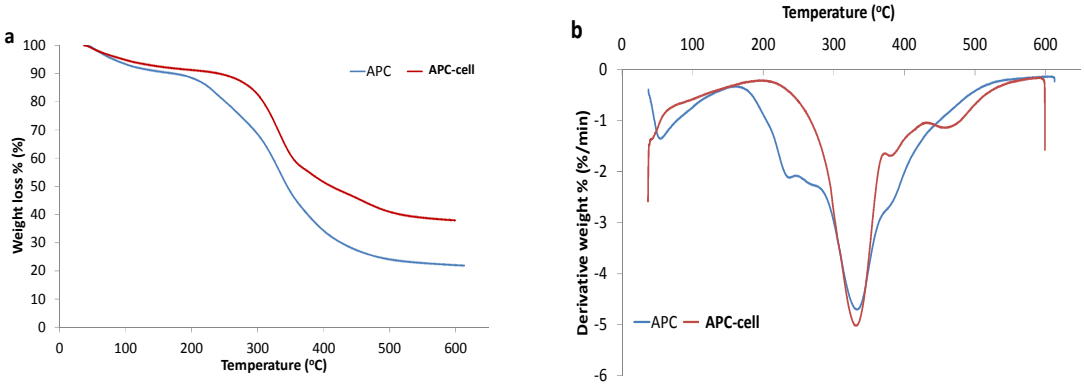

Figure 5: TGA thermograms (a) and DTG curves (b) of weight loss of APC and cellulose extracted from APC by $H_0PH_1E_p$ bleaching (APC-cell)

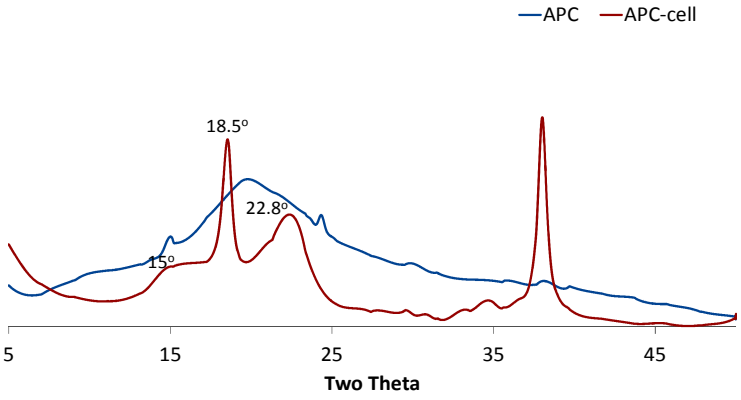

Figure 6: XRD patterns of APC and cellulose extracted from APC by $H_0PH_1E_p$ bleaching (APC-cell)

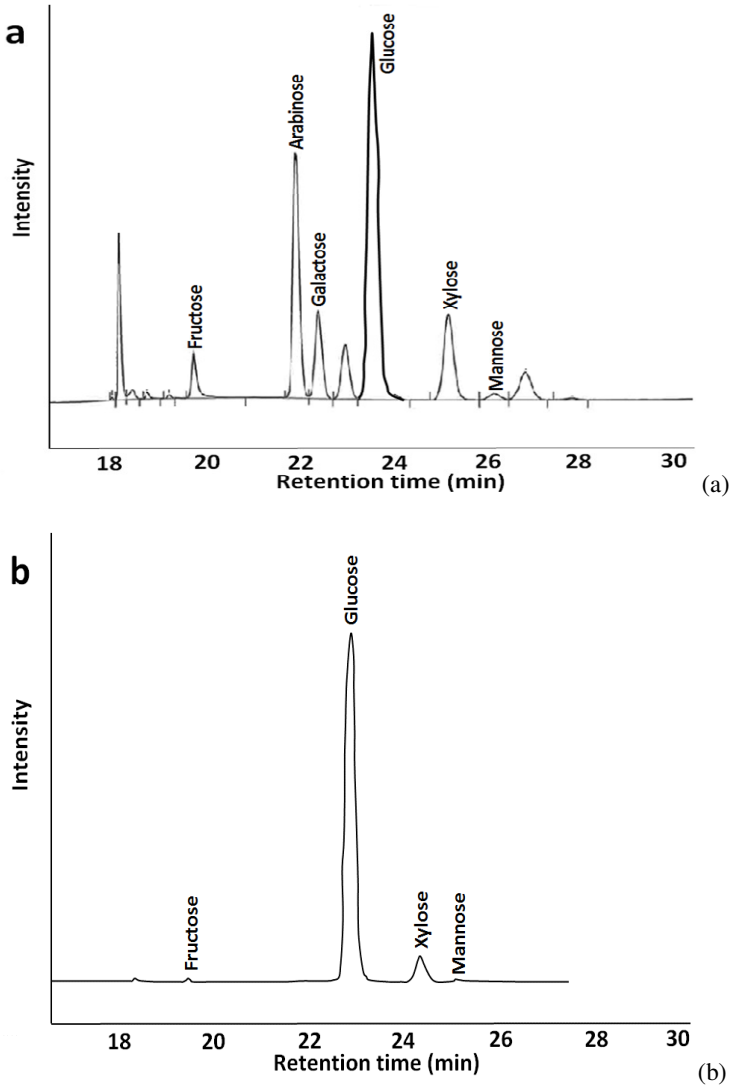

Figure 7: Sugar analysis from HPLC chromatograms of (a) APC and (b) cellulose extracted from APC by $H_0PH_1E_p$ bleaching (APC-cell)

Dissolution of APC-cell and its molecular weight investigation

GPC analysis was performed to investigate the molecular weight of cellulose extracted from APC via the $H_0PH_1E_p$ bleaching sequence. GPC analysis results are shown in Figure 8. Two molecular weight data, number average molecular weight (Mn) and weight average molecular weight (Mw), were calculated according to the reference.[17] The molar mass distribution is represented by the wavy line and the UV chromatogram is the dotted line. The Mn and Mw of APC-cell were determined to be 80.2 kDa and 219.9 kDa with a degree of polymerization (DP) of about 500. The DP is consistent with that shown in the literature for cellulose powder.[29,30] The polydispersity index (2.7) and the shape of the molar mass curve show a large fraction of APC-cell with low molecular weight. The DP of cellulose extracted from APC-cell is close to the range of commercial Avicel products (DP 300-500). However, as compared to other agricultural biomass wastes, the molecular weight of the cellulosic component from APC-cell is similar to that of the cellulosic component from bagasse, showing Mn of 125.6 kDa and Mw of 215.8 kDa,[31] but its DP is lower than that of the cellulosic component from corn stover in terms of different extraction methods, showing a DP ranging from 1250 to 2580.[32]

The cellulose used in the food and pharmaceutical industries is defined as powdered cellulose, which is a "purified, mechanically disintegrated cellulose prepared by processing bleached cellulose obtained as pulp from such fibrous materials as wood or cotton".[33] It shows an average fiber length from 22 to 120 µm and is generally used as filler in food and pharmaceutical products.[33] However, due to poor mouthfeel, microcrystalline cellulose (MCC) with reduced fiber length has greatly replaced the traditional powdered cellulose, such as Avicel® from FMC Biopolymer. These MCC products exhibit low molecular weight (DP: 300-500), small particle size (20-180 µm), improved mouthfeel, low moisture, improved flowability, and high tableting performance (FMC Biopolymer webpages). Comparably, the cellulose extracted from APC in this study shows potential for food and pharmaceutical applications due to its low DP, similar to that of MCC, its relatively low moisture content, and its relatively pure composition of glucose monomer. So, cellulose extracted from APC is qualified for use in the food and pharmaceutical industries without any further hydrolysis, as in the case of the cellulose extracted from other sources.

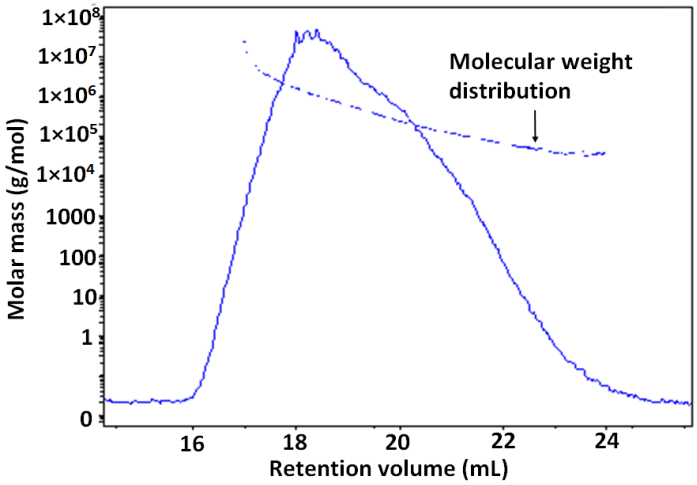

Figure 8: Molar mass distribution versus elution time for cellulose extracted from APC by $H_0PH_1E_p$ bleaching (APC-cell)

CONCLUSION

Alkaline pulping (Kraft pulping), combined with an $H_0PH_1E_p$ bleaching operation, was used in this study to extract and purify cellulose from argan press cake, a biomass resource known as agricultural waste. As compared to other extraction approaches, Kraft pulping followed by $H_0PH_1E_p$ bleaching operation led to the extraction of cellulose with high purity. Material characterization, sugar analysis, and molecular weight measurement of the extracted cellulose confirmed the quality and the purity of cellulose obtained from APC. In the light of the low cost of APC, the extracted cellulose may be deemed to be a potential value-added product for food and pharmaceutical applications.

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