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***CAMPUS* LARANJEIRAS DO SUL**
CURSO DE ENGENHARIA DE ALIMENTOS

DAVID FERNANDO DOS SANTOS

VALORIZAÇÃO DOS RESÍDUOS DA COLHEITA DE MILHO ATRAVÉS DA PRODUÇÃO DE NANOCELULOSE

LARANJEIRAS DO SUL – PR
2020

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Trabalho de conclusão de curso de graduação apresentado com requisito parcial para obtenção de grau Bacharel em Engenharia de Alimentos da Universidade Federal da Fronteira Sul.

Orientadora: Profª. Drª Vânia Zanella Pinto

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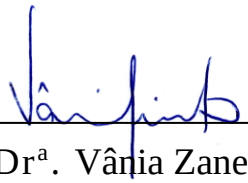

Prof. Drª. Vânia Zanella Pinto

Drª. Bárbara Biduski

Prof. Vinícius Gonçalves Deon

Dedico este trabalho aos meus pais que me proveram todo o suporte necessário para que um trabalho como este e outros fossem possíveis.
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“Então cerre os punhos, sorria
e jamais volte pra sua quebrada de mão e mente vazia”
– Emicida (Levanta e anda)

“Você pode brilhar, não importa do que seja feito!”
–O Grande Soldador (Robôs, 2005)

“When one dares to try, rewards are not guaranteed, but at least it is an adventure”
– Andre K. Geim

Lista de Figuras

SUMÁRIO

ESPECIFICAÇÕES DA REVISTA QUE SERÁ ALVO PARA A SUBMISSÃO

Este Trabalho de Conclusão de Curso será redigido em forma de um artigo de acordo com as normas da revista International Journal of Biological Macromolecules (ISSN: 1879-0003). As normas da revista que foi utilizada como base para a formatação se encontram no ANEXO I.

VALORIZAÇÃO DOS RESÍDUOS DA COLHEITA DE MILHO ATRAVÉS DA PRODUÇÃO DE NANOCELULOSE

AGGREGATING VALUE TO CORN CROP RESIDUES BY THE NANOCELLULOSE OBTAINTION

HIGHLIGHTS:

- Stalks, husk and corncobs were used to isolate cellulose and produce nanocellulose fibers by ball milling
- The isolation process reduces the cellulose fibers crystallinity
- The ball milling of 6h, 9h and 12h resulted in nanocellulose fibers
- 9 h of milling resulted in RC~60 %, size ~107 nm and small evidence of nanofibers agglomeration.

Resumo

A revalorização de resíduos é um tópico de interesse de diversas áreas da ciência, e vem sendo muito explorada na produção de nanocelulose, visto a quantidade de resíduos lignocelulósicos gerados por diversos setores agroindustriais. A nanocelulose mostra potencial de aplicações ilimitadas e produção crescente. Com isto, este trabalho busca avaliar a exploração de resíduos de colheita de milho com elevado teor de celulose (colmo, o sabugo e a palha do milho) para a obtenção de nanocelulose. Foram utilizados o isolamento e branqueamento químico e a fibrilação por moagem mecânica por 6h, 9h e 12h. As nanoceluloses produzidas foram avaliadas por espectrometria de infravermelho (FTIR), espalhamento dinâmico de luz, potencial zeta, difração de raios-X e espectrometria Raman. O isolamento e branqueamento se mostraram demasiadamente intensos reduzindo a cristalinidade dos materiais. A fibrilação se mostrou comportamento independente com relação a cristalinidade de cada material; o incremento do tempo de moagem gerou respostas diferentes para cada resíduo, aumentando e/ou diminuindo a cristalinidade em diferentes tempos. Em paralelo, as amostras demonstraram tamanhos em escala nanométrica e certa taxa de aglomeração devido a sua constituição química. A melhor condição de processamento foi o tempo de 9 horas de moagem para a amostra de palha de milho, gerando nanoceluloses com cristalinidade relativa superiores a 63% e uniformidade, raio hidrodinâmico médio de 121 nm, potencial zeta de -38 mV e cristalinidade relativa de 63,87 %. Estes materiais e processo e de obtenção de nanocelulose avaliados, mostraram-se eficientes e com potencial de aplicações reais em maior escala.

Palavras-chave: Cristalinidade relativa; Raio hidrodinâmico; Fibrilação por moagem mecânica.

Abstract

The waste revaluation is a topic of interest in science and has been widely explored to produce nanocellulose, showing the unlimited application potential and a production growing. This work evaluates the nanocellulose obtention from high cellulose content corn crop waste (stalk, cob and husk). To produce nanocellulose, were chosen the chemical isolation and bleaching and fibrillation by three different times (6h, 9h and 12h) of mechanical grinding. Nanocellulose were evaluated through the dynamic light scattering, zeta potential, infrared (FTIR) and Raman spectrometry, and X-ray diffraction. The isolation and bleaching showed to be too intense, reducing the relative crystallinity (RC). Fibrillation was independent in relation to the RC; the increase in the grinding time generated different responses, increasing and/or decreasing the RC. Also, the samples demonstrated nanometric scale sizes (107 – 335 nm of hydrodynamic radius) and a certain rate of agglomeration due to their chemical constitution. The 9h milling for the husk sample was the best processing condition, generating uniform samples, satisfactory RC (63.87%), hydrodynamic radius average of 121 nm, zeta potential of -38 mV. These materials and the nanocellulose obtention process evaluated were efficient and with potential for real applications on a larger scale.

Keywords: Relative crystallinity; Hydrodynamic radius; Fibrillation by ball milling.

1. INTRODUÇÃO

O milho é uma das primeiras plantas que foram domesticadas pelo homem, e atualmente um dos grão mais produzidos no mundo com a produção mundial crescendo ano à ano [1,2]. No Brasil a área plantada deste grão é de 4,1 milhões de hectares, com produção estimada para 2019/2020 de 26,3 milhões de toneladas [3]. No entanto, essa grande produção gera também uma grande quantidade de resíduos, entre 1,21 e 1,82 toneladas por hectare de colheita de milho, sendo divididos em colmos (50 %), folhas (20 %), sabugos (20 %) e palha (10%) [4]. Esses diferentes tipos de resíduo apresentam diferentes teores lignocelulósicos, marcados pela similaridade no teor de celulose, porém, com teores de hemicelulose e lignina divergentes [5–8].

Ao mesmo tempo, novas fontes de celulose vêm sendo alvo de pesquisadores e empresas, como uma alternativa para materiais derivados de madeira [9]. A exemplo disso, resíduos agroindustriais, como os da colheita de milho, têm um ciclo de crescimento mais curto e menor teor de lignina, comparados com as arvores [10]. As características desta matéria-prima criam novas possibilidades de aplicação, visto que as aplicações mais comuns desse resíduo são como cobertura e fonte de matéria orgânica para o solo, alimentação de animais na agropecuária [11], a produção de biodiesel [12–15], e mais recentemente e em escala experimental na produção de nanocelulose [2,15–21].

Com propriedades superiores comparadas às fibras convencionais de celulose, a nanocelulose possui pelo menos uma das dimensões em tamanho nanométrico e com isso elevada área superficial [22]. A nanocelulose pode ser classificada em três tipos, nanofibras de celulose, nanocristais de celulose e nanocelulose bacteriana, tendo diferentes propriedades e vantagens [23–25]. Essas diferentes classificações estão relacionadas ao método de produção e morfologia, os nanocristais e nanofibras são os mais comuns e além de diferentes dimensões apresentam diferente cristalinidade, os nanocristais apresentam cristalinidade relativa próxima a 73 - 86% enquanto as nanofibras 45 - 71 % [26–29]

Para o ano de 2020 é estimada uma produção global entre 2.500 e 5.500 toneladas de nanomaterial [24]. A produção da nanocelulose é baseada em duas etapas, o pré-tratamento, ou isolamento das fibras de celulose e a fibrilação destas fibras. Na etapa de isolamento das fibras, a lignina e outros compostos minoritários são removidos da matéria-prima. Na etapa de fibrilação as estruturas celulósicas são reduzidas a uma escala nanométrica por meio de um processo enzimático, químico ou físico, sendo o tratamento químico com ácidos fortes concentrados o método mais utilizado [24,30,31].

A utilização de resíduos é uma importante alternativa como um processo de produção mais amigável ao meio-ambiente, reduzindo o impacto industrial no meio ambiente. Para aumentar a viabilidade desse processo se mostra importante o desenvolvimento de métodos para focados em resíduos gerados na região produtora, reduzindo assim os custos de transporte do resíduo [32], e equilibrando o alto custo de produção, o qual permanece sendo um problema para a comercialização da nanocelulose [15]. As pesquisas sobre a produção desse material já foram realizadas com resíduos de banana [33–35], palmeira do pupunha [36], lima [37], erva-mate [38], soja [29,39,40], resíduos industriais da produção de vinho [41] e cerveja [42], e também os resíduos da colheita de milho [2,7,9,17,19,43,44].

A obtenção de nanocelulose por meio de moagem mecânica é uma técnica que foi muito estudada em busca de um método energeticamente eficiente e sustentável. Porém, a dificuldade de controle dos parâmetros e resultados se mostrou um desafio. Com isto, este trabalho buscou produzir nanocelulose de resíduos da colheita de milho, sendo estes o colmo da planta, o sabugo e a palha da espiga, por meio de método físico de fibrilação e caracterizar as suas propriedades físicas.

2. MATERIAIS E MÉTODOS

2.1 MATERIAIS

Os resíduos do colmo da planta, sabugo e palha da espiga de milho foram coletados manualmente em uma propriedade rural na cidade de Camargo, Rio Grande do Sul. Estes foram então secos (50 °C, 24 h), e posteriormente moídos em moinho de facas tipo *Willye* (Fortinox, Start FT-50, Brasil).

O clorito de sódio foi adquirido da Sigma Aldrich (São Paulo, SP), o ácido acético, etanol e hidróxido de sódio foram adquiridos da Labsinth (Diadema, SP). Todos os demais reagentes utilizados são de grau analítico.

2.2 ISOLAMENTO DAS FIBRAS DE CELULOSE

Primeiro as fibras de celulose foram isoladas com a remoção da lignina e da hemicelulose utilizando tratamento alcalino. Utilizou-se solução de hidróxido de sódio (4%, m/v) soba agitação mecânica e aquecimento (80 °C) por 4 horas. Após, a suspensão formada foi neutralizada com ácido acético (3 %, v/v) e lavada com excesso de água destilada; esse processo se repetiu mais três vezes. A segunda etapa baseou-se no branqueamento das fibras isoladas (10 %, m/v) com uma mistura (1:1) de clorito de sódio ($NaClO_2$) (1,7%, v/v) e tampão de acetato de sódio (pH 4,5). A mistura foi submetida a agitação sob aquecimento (70 °C) durante 4 horas; então, a amostra foi filtrada em funil de Büchner, lavada com água destilada em excesso, e seca em estufa (50 °C, 24 h); esse processo se repetiu duas vezes. Este processo apresentou um rendimento de 37%, 36% e 37% para os resíduos de colmo, sabugo e palha de milho, respectivamente, as fibras isoladas também apresentaram coloração branca, indicando a remoção da lignina e hemicelulose, posteriormente comprovada pela caracterização.

2.3 PRODUÇÃO DA NANOCELULOSE

Para a produção da nanocelulose foi utilizada moagem mecânica por meio de um moinho para jarros (MA2301 Marconi, Piracicaba, SP) com esferas e jarros de alumina, com volume de 1 litro e diâmetro e altura de 150 mm e 195 mm, respectivamente. Aproximadamente 4 g de fibras isoladas de cada resíduo foram depositadas no jarro juntamente com 4 mL de uma solução de água destilada:etanol (80:20) e bolas de alumina na proporção de 244 g grandes (diâmetro de 21 mm) e 44 g pequenas (diâmetro de 12 mm), procedendo para a moagem durante 6, 9 e 12 h. Após a moagem as amostras foram secas à 50 °C por 12 h.

2.4 CARACTERIZAÇÃO DA NANOCELULOSE

2.4.1 Espalhamento dinâmico de luz (DLS) e potencial zeta (ξ)

O DLS foi performado utilizando um equipamento ALV/CGS-3 (ALV-GmbH, Alemanha) equipado com um laser polarizado de HeNe (22mW), operando no comprimento de onda (λ) 633 nm, num ângulo estático de 90° para o DLS. Para esta caracterização as amostras foram diluídas em água destilada à 0,01 % (m/v).

O potencial zeta (ξ) foi aferido utilizando um equipamento Zetasizer Nano-ZS (Malvern Instruments, Reino Unido), configurada para uma leitura de 10 s, avaliando a mobilidade eletroforética das partículas convertida em potencial zeta. Para esta caracterização as amostras foram diluídas em água destilada à 0,01 % (m/v)

2.4.2 Espectroscopia de infravermelho com transformada de Fourier (FTIR)

Os espectros de infravermelho foram obtidos para as amostras secas de colmo, sabugo e palha de milho secas e posteriormente as fibras de celulose isoladas, e para as diferentes amostras de nanocelulose foram obtidos utilizando um espectrofotômetro equipado com acessório de refletância total atenuada (Frontier 94942 PerkinElmer, EUA). Os espectros foram obtidos na região de 400-4000 cm^{-1}, após 32 leituras em uma resolução de 4 cm^{-1} e normalizados no pico de 899 cm^{-1} que é o pico referente à ligações β-glicosídicas entre anéis de anidroglucose da celulose [27,45–49]

2.4.3 Espectroscopia Raman

As matérias primas, fibras de celulose isoladas e amostras de nanocelulose foram caracterizadas quanto a espectroscopia Raman (XRD Raman Spectroscopy Thermo Scientific, EUA), foram utilizados aproximadamente. O sistema utilizado opera com uma fonte de laser de 780 nm e 5,0 mW. Os espectros foram obtidos em três diferentes pontos da amostra com magnetização de 50x, numa faixa de 100 – 4000 cm^{-1}, com 32 leituras e uma resolução de 4 cm^{-1}. Todos os gráficos tiveram a linha de base corrigida, com 25 pontos, utilizando o programa OriginPro 8.5.

2.4.4 Difração de Raios-X (DRX) e cristalinidade relativa (RC)

As amostras de celulose isoladas dos resíduos de milho e de suas respectivas nanocelulose produzidas foram caracterizadas utilizando um difratômetro de raios-X D8 Focus (Bruker AXS – Karlsruhe, Alemanha), operando à 40 kV e 40 mA, com radiação

monocromática CaKαl (λ = 1.54056 Å), selecionada por um monocromador de cristal curvado de Ge (111). Os dados foram obtidos de 10° a 80° com passo de 0,01° e intervalo de leitura de 100 s para cada 0.5°. Para a cristalinidade relativa utilizou-se a Equação 1, do método de Segal [50], que relaciona a o pico cristalino e a intensidade de difração do material não-cristalino.

$$RC\ (\%) = \frac{(I_{200} - I_{am})}{I_{200}} \times 100 \qquad (1)$$

Sendo:

$CR\ (\%)$: cristalinidade relativa;

I_{200}: intensidade do pico cristalino, 22°;

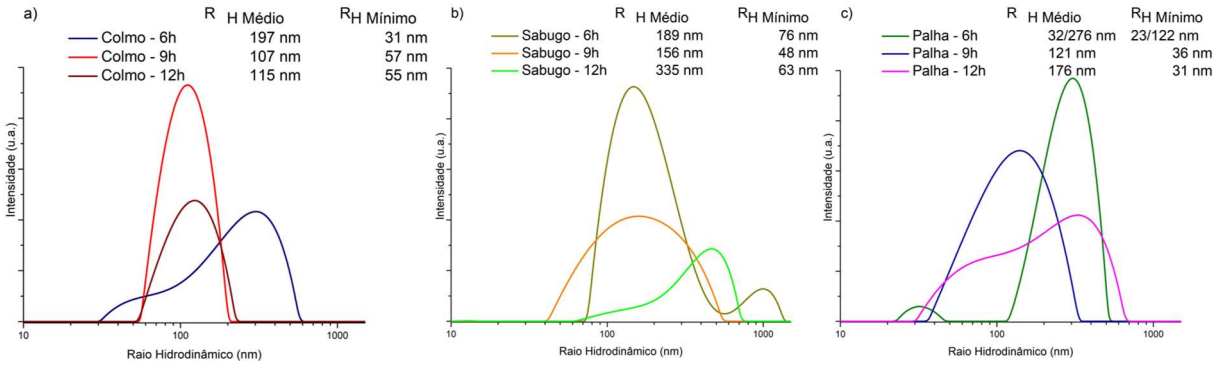
I_{am}: intensidade da região amorfa, 18,5°.

3. RESULTADOS E DISCUSSÃO

3.1 ESPALHAMENTO DINÂMICO DE LUZ (DLS) E POTENCIAL ZETA

O DLS das amostras de celulose demonstra os diferentes raios hidrodinâmicos das amostras (Figura 1). O tempo de moagem de 9 horas apresentou os menores raios hidrodinâmicos médios para todos os diferentes resíduos, sendo que o colmo da planta de milho apresentou o menor raio médio dentre todas as amostras (107 nm).

Figura 1 – Raio hidrodinâmico das partículas de nanocelulose com diferentes tempos de moagem.



Observando a Figura 3 é possível visualizar também o comportamento de aglomeração em algumas amostras, com picos alargados e não definidos, principalmente as amostras de 12 horas de moagem oriundas de sabugo (Figura 1b) e palha de milho (Figura 1c) e a amostra de 6 horas de moagem de colmo de milho (Figura 1a). O deslocamento para a direita do raio hidrodinâmico médio indicando um tamanho médio das partículas mais elevado, mesmo essas amostras apresentando a dimensão mínima para a amostra de sabugo (63 nm sabugo 12 h) e para a amostra de palha (31 nm 12 h) e colmo (31 nm 6 h). Isso pode ser considerado um sinal de aglomeração destas partículas na suspensão utilizada para esta caracterização. O comportamento polidisperso ocorre durante o processo de moagem pela formação de uma película do material moído nas bolas adicionadas ao jarro do moinho, que reduz então a energia no processo, e que, por sua vez, reduz a eficiência de quebra de regiões amorfas e produz estruturas de dimensões maiores [49,51].

Estes fenômenos de aglomeração descritos para o DLS podem ser relacionados aos resultados de potencial zeta apresentados na Tabela 1. Considera-se a suspensão de nanocelulose estável desde que apresente resultado em módulo acima de 30 mV e que a aglomeração deve ocorrer em módulos inferiores a 15 mV [52]. Avaliando os diferentes tempos de moagem para as amostras de colmo, é possível identificar o incremento do potencial zeta

com o incremento do tempo de moagem, corroborando com os resultados da Figura 1 (a). A maior presença de aglomeração no tempo de 6h (-15,5 ± 1,3 mV) próximo ao módulo de aglomeração, e picos bem definidos e levemente alargados para as amostras de 9 e 12 horas de moagem indicando que a eficiência destes tempos na obtenção de nanocelulose.

Nas demais amostras, de sabugo e palha, a tendência de aglomeração é evidente pelos dados de DLS (Figura 1 (b) e (c)). Entretanto, ao comparar estes resultados com os valores de potencial zeta, a amostra de sabugo 6h (-13,8 ± 1,2 mV) apresentaria este perfil de aglomeraçãoCom isto, a nanocelulose dos resíduos de palha e sabugo de milho apresentam perfil de aglomeração com módulos de potencial zeta superiores a 30 mV. De acordo com Liu et al. [17], isto ocorre visto que a celulose em suspensão pode gerar uma grande tensão superficial devido aos grupamentos hidroxila presentes em sua estrutura, que então pode favorecer a aglomeração das partículas em busca de estabilização por meio de ligações de hidrogênio. Condizendo com os espectros de infravermelho das amostras antes e depois do isolamento das fibras de celulose de sabugo e palha (Figura 1 (b) e (c)), que apresentaram o incremento de intensidade na banda relacionada a hidroxila após o isolamento, enquanto o resíduo de colmo apresentou redução desta banda. Então a observação feita por Liu et.al. [17] corrobora com os dados das amostras de nanocelulose produzidas a partir de resíduos de palha e sabugo de milho (Figura 1, Tabela 1).

Tabela 1 – Potencial zeta da nanocelulose produzida de resíduos da colheita de milho.

Resíduo	Tempo de moagem (h)	Potencial Zeta (mV)
Colmo	6h	-15,5
	9h	-18,4
	12h	-41,8
Sabugo	6h	-13,8
	9h	-34,7
	12h	-42,0
Palha	6h	-30,5
	9h	-38,0
	12h	-36,7

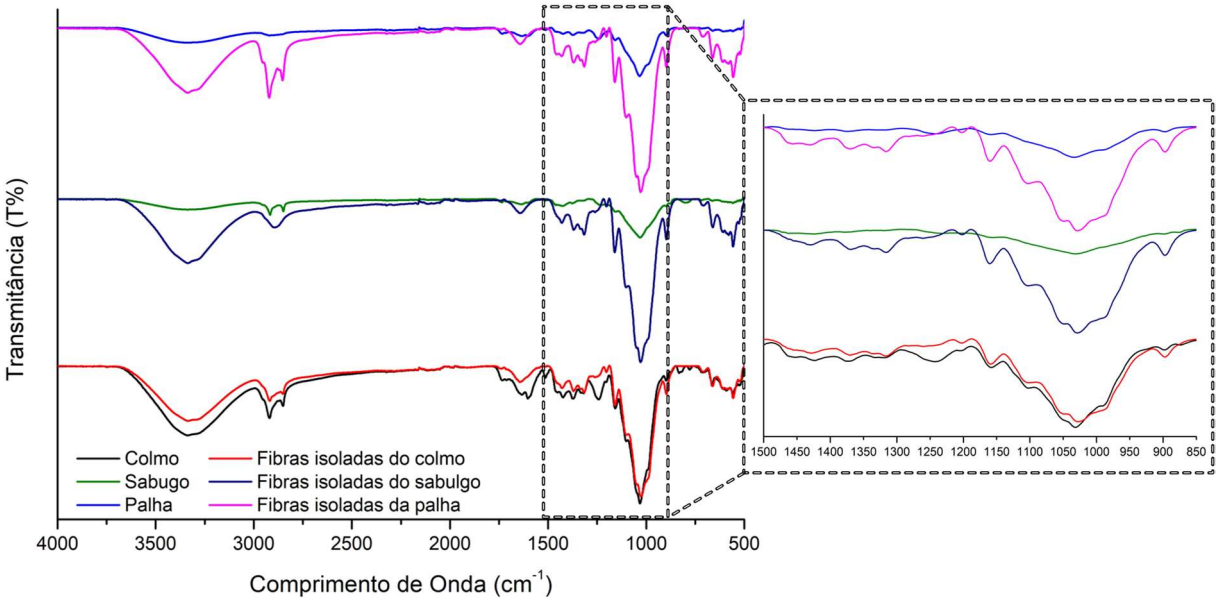
*Médias de triplicatas.

3.2 ESPECTROSCOPIA DE INFRAVERMELHO COM TRANSFORMADA DE FOURIER (FTIR)

Os espectros das amostras de resíduos de milho antes e após o isolamento estão apresentados na Figura 2. Estes espectros apresentam bandas características de um material lignocelulósico. Este padrão se deve a composição destes resíduos, visto que o colmo da planta de milho apresenta teores de celulose de 32,40% a 38,50% [5,6], enquanto os sabugos 43,20% a 31,20% de celulose [5,7], e a palha da espiga cerca 21,80% a 40,60% [8,53]. Os maiores teores de lignina encontrados na literatura são para o resíduo de palha de milho (16% a 20%), seguidos pelo sabugo de milho (14% a 17%) e o colmo (2,5% a 15%), com relação a hemicelulose todos apresentaram teores entre 28% e 41% [5–8,53]

As bandas características das fibras de celulose indicam a eficiência do processo de isolamento e branqueamento. sendo 3400, 2900, 1460, 1428, 1370, 1330, 1160, 1110, 1050, 890 cm^{-1}, que correspondem à vibração da ligação –OH, vibração e estiramento C–H, ligação assimétrica C–H_3, ligação simétrica CH_2, vibração da ligação CH_2, Ligação –OH, vibração assimétrica C–O–C, ligações β-glicosídicas (C-O-C), vibração C–O–C do esqueleto do anel de piranose da celulose, e ligações β-glicosídicas entre anéis de anidroglucose da celulose, respectivamente [7,27,58,59,45–47,49,54–57] [60]. Como indicativo do isolamento da celulose as bandas que representam a hemicelulose e lignina também são importantes, sendo 1730, 1515, 1245 e 1230 cm^{-1}, que correspondem ao grupo acetil e ester urônico da hemicelulose, componentes fenólicos da lignina, vibração de estiramento da hemicelulose, e vibração do anel aromático da lignina, respectivamente [27,45,46,49,58] [60].

Figura 2 – Espectro infravermelho das amostras resíduos da colheita de milho antes e depois do isolamento.

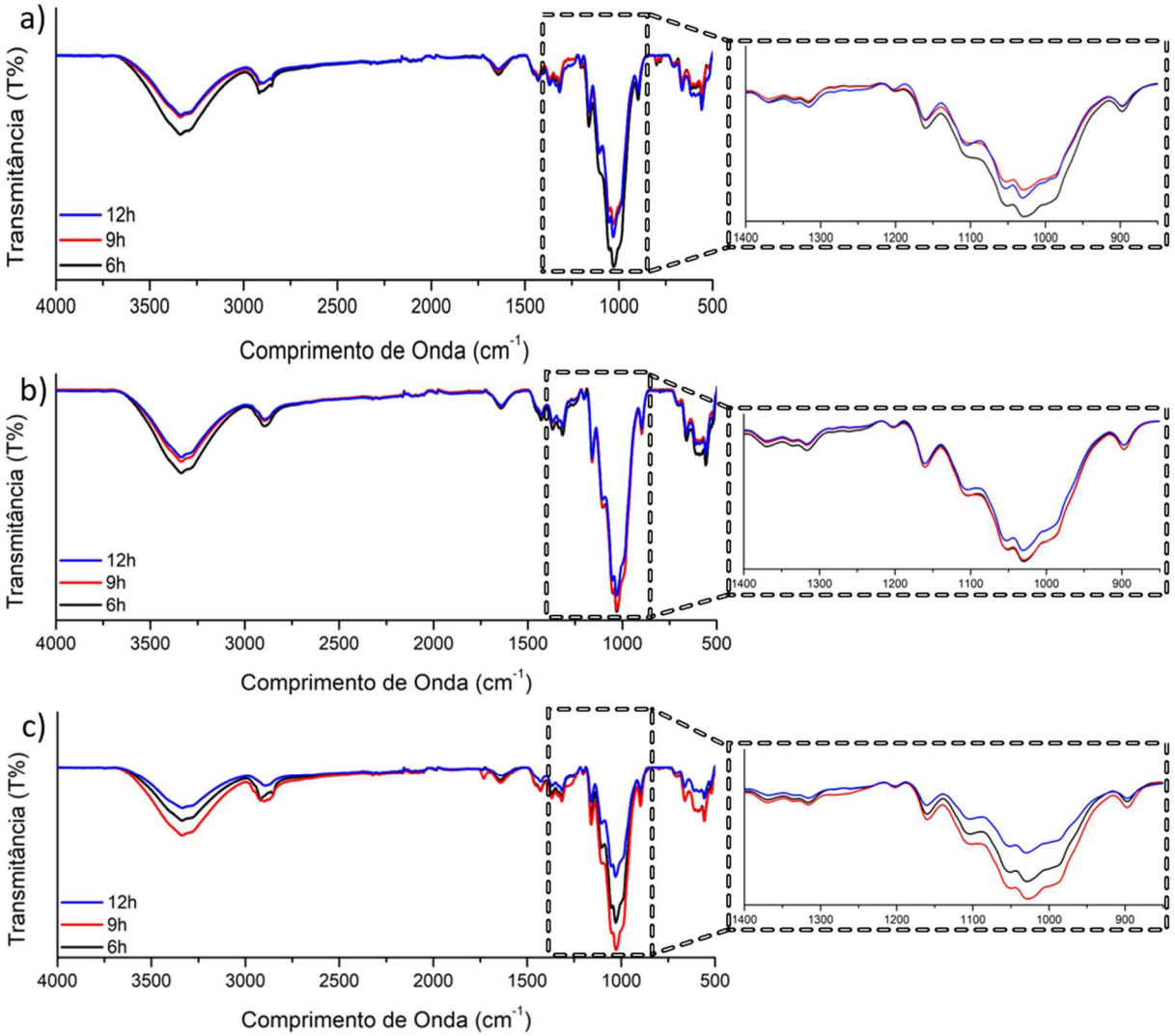


Nos espectros das amostras de palha e sabugo é notável a melhor definição das bandas características da celulose e a redução da intensidade das bandas de lignina e hemicelulose, que pode ser um indicativo da eficiência do processo de isolamento da celulose [61]. Porém, a amostra do colmo da planta antes e após o isolamento das fibras de celulose não apresentaram alterações evidentes na resolução das bandas referentes à celulose, mas há redução das bandas referentes a hemicelulose e lignina (1730, 1515, 1245 e 1230 cm^{-1}). Desta forma, percebe-se que o resíduo de colmo apresenta maior teor inicial de celulose que pode ser devido às características intrínsecas do resíduo e as diferenças estruturais da planta.

Os espectros das amostras de nanocelulose produzidas por fibrilação mecânica (Figura 2), apresentam grande similaridade com o perfil espectral das amostras de resíduos(Figura 2). O processo de moagem das fibras de celulose pode gerar uma característica amorfa na celulose conforme o incremento do tempo de processamento, e com isto algumas bandas relacionadas a celulose podem apresentar mudança de intensidade [62–64]. Khan e seus colaboradores [62] avaliaram o impacto da moagem mecânica por 1h no pré-tratamento de celulose cristalina, e descrevem mudanças no perfil do espectro de FTIR com o aumento na região cristalina do material. As alterações observadas por eles foram o alongamento e redução de intensidade nas bandas de 2900 cm^{-1} e 899 – 1500 cm^{-1} e o aumento da intensidade na banda de 898 cm^{-1}. A região de 1270 – 1800 cm^{-1}, corresponde a organização da estrutura de materiais celulósicos e é característica da nanocelulose cristalina, ou seja, sua redução de intensidade relaciona-se com a redução de cristalinidade da amostra [61]. Estes fenômenos foram observados nos três grupos

de amostra de nanocelulose estudados, e foram relacionados com a alteração na cristalinidade e comprovados posteriormente pela difração de Raios-X [62].

Figura 3 – Espectro infravermelhos das amostras de nanocelulose dos resíduos de colmo (a), sabugo (b) e palha (c) de milho com diferentes tempos de moagem

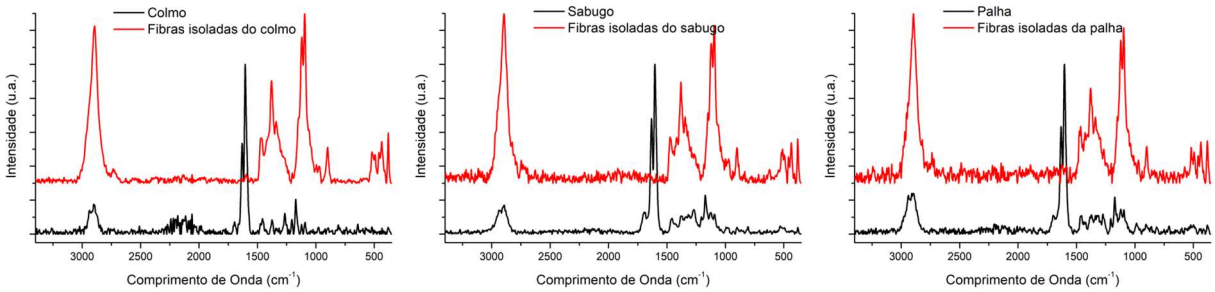


3.3 ESPECTROSCOPIA RAMAN E ÍNDICE DE CRISTALINIDADE (IC)

A espectroscopia Raman, se mostra uma técnica eficiente para avaliar os teores de celulose tipo I e tipo II. A celulose tipo I é um polímero que apresenta estrutura organizada em camadas pelas interações hidrofóbicas, enquanto que a celulose tipo II apresenta a estrutura organizada em uma rede tri-dimensional pelas pontes de hidrogênio e com uma energia potencial maior [65]. Os espectros Raman dos resíduos utilizados e suas fibras isoladas (Figura 4) indicam o incremento no teor de celulose nas amostras após o isolamento, visto que os dois picos característicos de 1098 e 2900 cm^{-1} (relacionados as vibrações das ligações C–O e C–C e

C–H, respectivamente), ganharam um incremento em sua intensidade e resolução[66]. Os espectros também indicam a presença de celulose do tipo II, pelo aumento na intensidade e nitidez dos picos em 577 e 1462 cm^{-1}, nas fibras isoladas [66,67]. Os espectros das fibras isoladas apresentam a ausência de bandas presentes nos resíduos na região de 1500 – 1800 cm^{-1}, que é uma região característica das ligações C=C e C=O dos anéis aromáticos presentes na lignina [68,69], a remoção desta banda no espectro das fibras isoladas indica o sucesso da remoção da lignina durante o processo de isolamento. Constata-se também a presença de regiões cristalinas no resíduo antes e depois do isolamento, visto que a nitidez e intensidade de picos indica a natureza cristalina do material [20], corroborando com os resultados de RC (Tabela 2), independentemente da redução de RC após o isolamento para as amostras de colmo e sabugo, com cristalinidade superior a 44% para todos os resíduos e fibras isoladas.

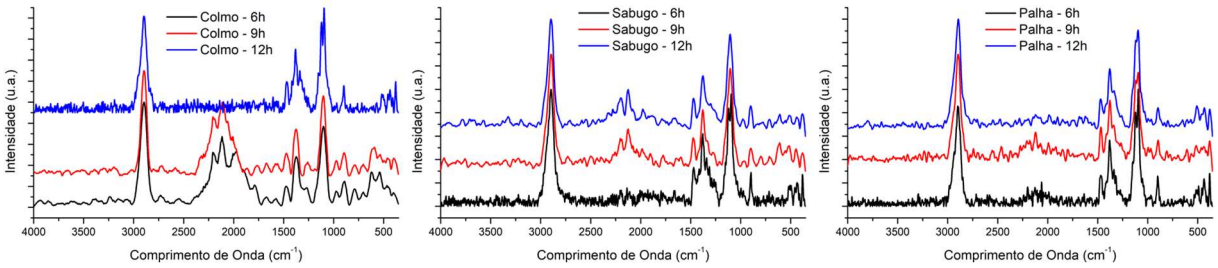
Figura 4 – Espectro Raman dos resíduos da colheita de milho antes e depois do isolamento.



Como nas fibras isoladas, constata-se a presença dos picos característicos da celulose (1098 e 2900 cm^{-1}) em todas as amostras de nanocelulose (Figura 5), porém, com melhor nitidez. Este aumento na nitidez dos picos é um indicativo de uniformidade e organização da estrutura do material. Esta característica é demonstrada também pela redução do pico de 900 cm^{-1}, que é associado a desordem do material [67].

Nas amostras de colmo, percebe-se o incremento na intensidade dos picos da celulose tipo II (577 e 1462 cm^{-1}) que condiz com o aumento na cristalinidade (Tabela 2) e potencial zeta (Tabela 1) deste material com decorrer do aumento do tempo de moagem, convertendo a celulose tipo I em tipo II.

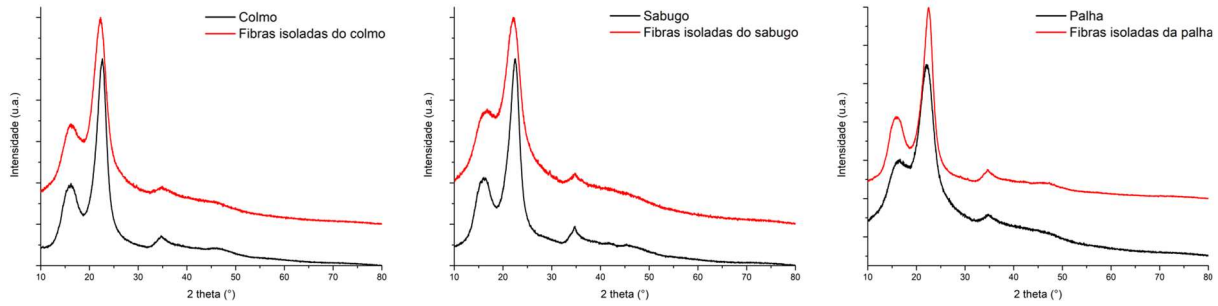
Figura 5 – Espectro Raman das amostras de nanocelulose dos resíduos da colheita de milho com diferentes tempos de moagem.



3.4 DIFRAÇÃO DE RAIOS-X (DRX) E CRISTALINIDADE RELATIVA (RC)

Na Figura 4 estão apresentados os difratogramas de raios-X das amostras de resíduos antes e após o isolamento das fibras de celulose. Para os diferentes resíduos há presença de picos nos ângulos 2θ 15,6°, 22,7° e 34,6°, picos reconhecidos como característicos da celulose cristalina [70].

Figura 6 – Difratograma de Raios-X dos resíduos da colheita de milho antes e depois do isolamento.



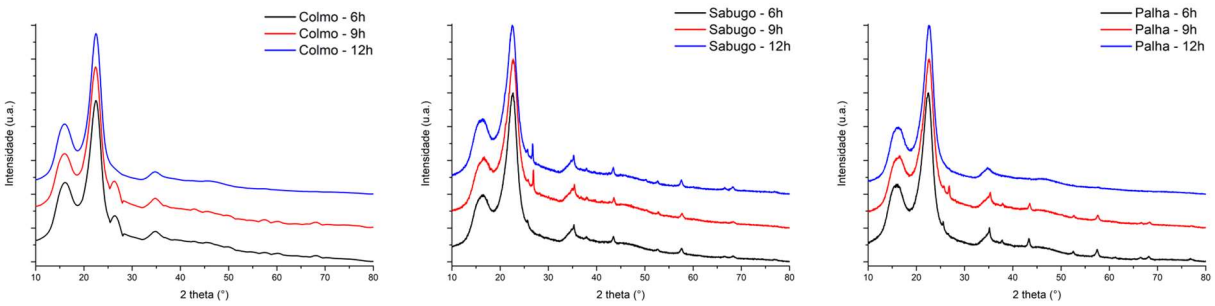
Durante o processo de isolamento das fibras de celulose espera-se a remoção de uma parcela significativa de lignina e hemicelulose, assim obtendo as fibras de celulose com elevado grau de pureza. Considerando que a celulose tipo I tem característica de ser um material cristalino, e a lignina e hemicelulose serem materiais amorfos, com o isolamento é esperado o aumento no índice de cristalinidade das amostras [7,54,71]. Na Tabela 2, estão apresentados os resultados de cristalinidade relativa dos resíduos antes e depois do isolamento. O resíduo de palha apresentou incremento de 49,00% para 69,78%, indicando um processo de isolamento eficiente em termos de cristalinidade. As demais amostras apresentaram a redução da cristalinidade relativa após o processo de isolamento, com redução de 70,88% para 56,62% para a amostra do colmo e de 66,84% para 44,47% para a amostra de sabugo. Esse comportamento

é contrário aos resultados esperados e mostra-se um indicativo de que o processo de isolamento foi mais intenso que o necessário, atingindo também as regiões cristalinas da amostra [7,72,73].

Tabela 2 – Cristalinidade relativa dos resíduos da colheita de milho antes e depois do isolamento e da nanocelulose produzida em diferentes tempos de moagem.

Resíduo	Etapa do processo	Cristalinidade relativa (%)
Colmo	Resíduo	70,88
	Fibras de celulose	56,62
	NM 6h	61,87
	NM 9h	63,75
	NM 12h	69,80
Sabugo	Resíduo	66,84
	Fibras de celulose	44,47
	NM 6h	64,95
	NM 9h	60,77
	NM 12h	62,83
Palha	Resíduo	49,00
	Fibras de celulose	69,78
	NM 6h	65,39
	NM 9h	63,87
	NM 12h	69,73

Figura 7 – Difratograma de Raios-X das amostras de nanocelulose dos resíduos da colheita de milho com diferentes tempos de moagem.



Esse perfil no difratograma das amostras de nanocelulose (Figura 5) indica modificação na estrutura e cristalinidade da celulose nas amostras como consequência da intensidade da moagem. As amostras de nanocelulose do colmo, apresentam um perfil nitidamente diferente

dos das amostras de sabugo e palha, a nanocelulose do colmo apresenta um incremento da RC relacionado ao incremento do tempo de moagem de 61,87% a 69,80%, para 6 e 12 horas respectivamente. As fibras isoladas da planta e sabugo apresentaram um incremento na RC após 6 horas de moagem de 5% e 20%, respectivamente, e no tempo de 9 horas ambas as amostras apresentam RC entre ~60% e ~64%, sendo uma redução de RC. Em 12 horas de moagem os resultados foram de ~70% para a palha e ~63% para o sabugo. Diversos estudos analisam a influência do tempo de moagem na cristalinidade da nanocelulose produzida e constatam a interação entre o tempo de processamento e a redução da cristalinidade relativa da amostra [20,62–64,74–76]. Em casos como a amostra de colmo que teve o incremento de sua cristalinidade, sugere-se que houve a transformação de celulose tipo I para tipo II durante o processo, que apresenta maior cristalinidade, assim aumentando sua RC e seu carga eletronegativa (Tabela 1) [76]. Em casos como das amostras de sabugo e palha, que apresentam uma redução da amostra de 6 horas para 9 horas seguido pelo incremento novamente em 12 horas, sugere-se que de 6 à 9 horas ocorre uma amorfização já prevista para este tipo de fibrilação [62,63], e à12 horas, ocorre quebra da região cristalina de maneira suficiente ao ponto que ela se sobrepõe à região amorfa [20]. Estes resultados estão de acordo com o previsto na discussão do espectro infravermelho das amostras de nanocelulose que relaciona a intensidade do processo com uma certa amorfização da nanocelulose produzida (Figura 3).

4. CONCLUSÃO

Pode-se concluir que todos os resíduos demonstraram potencial para a produção de nanocelulose, com diferentes propriedades obtidas o que possibilita diferentes aplicações para estes materiais. Os resíduos utilizados inicialmente apresentaram características diferentes, porém ao longo do processamento e incremento do tempo de moagem suas características iniciam a assemelhar-se.

Foi possível avaliar as influências da moagem na nanocelulose produzida. Houve incremento da cristalinidade das amostras de colmo e sabugo e redução da RC da amostra de palha após 6 horas de moagem, seguido pelo incremento da RC da amostra de colmo e redução de cristalinidade para todas as amostras de sabugo e palha após 9 horas de moagem, e incremento de RC para todas as amostras após 12 horas de moagem, atingindo 69,8%. houve incremento da cristalinidade das amostras de colmo e sabugo e redução da RC da amostra de palha após 6 horas de moagem, seguido pelo incremento da RC da amostra de colmo e redução de cristalinidade para todas as amostras de sabugo e palha após 9 horas de moagem, e incremento de RC para todas as amostras após 12 horas de moagem. Houve maior aglomeração das amostras com o incremento do tempo de moagem, resultando em raios hidrodinâmicos médio distorcidos comprovado pela análise de espalhamento dinâmico de luz e pelo potencial zeta. Com tudo, pode se afirmar que 9 horas de moagem foi a melhor condição de processamento visando uma cristalinidade relativa satisfatória (~60 % a ~64 %), uniformidade no tamanho médio das partículas (107 nm a 156 nm) e aglomeração das estruturas reduzida, juntamente com um potencial zeta acima do limite de aglomeração (18,4 a 38,0 mV).

O resíduo que apresentou melhores resultados para todos os diferentes tempos de moagem foi o resíduo de palha de milho, que a pesar de apresentar maior dispersão no perfil do espalhamento dinâmico de luz, obteve um raio hidrodinâmico médio de 121 – 276 nm, um potencial zeta de -30,5 a -38,0 mV, e uma cristalinidade relativa de 63,87 – 69,73 %. Assim, nanocelulose com melhor desempenho foi a de palha de milho com moagem de 9 horas, que apresentou raio hidrodinâmico médio de 121 nm, potencial zeta de -38 mV e cristalinidade relativa de 63,87 %.

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[5] Cancer Research UK, Cancer statistics reports for the UK. http://www.cancerresearchuk.org/aboutcancer/statistics/cancerstatsreport/, 2003 (accessed 13 March 2003).
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