Extraction of Nanocrystals from Millet (*Eleusine Coracana*) Husk Waste : Optimization using Box Behnken Design Method in Response Surface Methodology (Rsm)

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Abstract

Cellulose nanocrystals (CNCs) have unique and diverse applications in the various fields of developing nanomaterials. In this work, cellulose nanocrystals were extracted from millet husk residue waste using a homogenized acid hydrolysis method. The effects of the process variables namely; homogenization speed, acid concentration and acid to cellulose ratio on the yield and swelling capacity were investigated and optimized using the Box Behnken design method in response surface methodology. The cellulose and nano-cellulose obtained were characterized using transform infrared microscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The numerical optimization analysis results showed that the maximum yield of CNCs from cellulose was 93.12 % and obtained at homogenization speed, acid concentration, and acid to cellulose ratio of 7464.0 rpm, 63.40 wt %, and 18.83 wt % respectively. The maximum swelling capacity of 2.81 % was obtained at homogenization speed, acid concentration, and acid to cellulose ratio of 8000 rpm, 62.5 wt %, and 25 wt % respectively. A mathematical model was obtained to predict the yield and the swelling capacity of cellulose nanocrystals with R^2 of the value of 98.9 % and 97.9% respectively. The TGA showed that the thermal stability of cellulose was higher than that of CNCs, FTIR results showed functional groups of CNCs and cellulose were similar, SEM image of CNCs is porous and displayed narrow particle size and needle-like morphology as compared to cellulose and XRD pattern presented an increase in the intensity of CNCs.

1. Introduction

In nanotechnology, the modification and synthesis of nanomaterials with distinct configurations and functions are gaining increasing interest due to their multiples potential uses which are applicable in nanocarriers, packaging materials, cosmeceutical, drug delivery systems, biomaterials, water treatment, and food components (Leszczy et al. 2018; Niamsap et al. 2019). However, most of the chemicals used in the production of nanomaterials come from petroleum-derived resources which are toxic and detrimental to the environment. Alarms about global warming towards attaining sustainable development are of great concern and there is a critical need to substitute the traditional non-renewable materials with renewable resources (Onur et al. 2018). Also, the ability to convert abundant and cheap materials to produce high-value products offers great benefits.

Renewable energy is by the future the fastest-growing fuel source and giving about 14% of principal energy (Abdelraof et al. 2019). Cellulose fibers synthesized from animals, plants, and bacteria are the most available resources that can be used as renewable materials. Cellulose is the furthestmost specific kind of linear homopolymer produced in billions of tons yearly, consisting of β -D glucopyranose (1 $\rightarrow$ 4) fused through the hydrogen bonds (Lei et al., 2019). Cellulose predominately exists in the cell walls of plants and is crucial for the rigidity of the cell wall (Hynninen et al. 2019). Cellulose is applied in many applications because it is stable, biodegradable, environmentally friendly, and readily available (Awang et al. 2019).

In modern years, the use of cellulose has been in the areas of nanotechnology materials (Du et al. 2019). Acidic/alkaline hydrolysis extraction methods with sulfuric acid proceeds with the removal of more amorphous regions within the structures of cellulose, while the crystalline parts called nanoparticles were undamaged (Wu et al. 2018). Cellulose nanocrystals can be produced via alkaline/acidic hydrolysis, steam explosion, enzymatic hydrolysis, high-pressure symmetry, sonication, and grinding processes (Hemmati et al. 2018; Du et al. 2019),

The physicochemical features of cellulose nanocrystals can differ depending on the technique of extraction and the source of cellulose. Cellulose nanocrystals have been extracted from by alkali/hydrolysis methods using wall nutshells, banana peels, palm date fiber, sawdust, sago seed, and waste paper (Hemmati et al. 2018; Meng et al. 2019; Shafiei et al. 2010; Oyewo et al. 2019; Purushothaman, 2016; Souza et al. 2017).

The two major millets that are grown in Sub-Saharan Africa are the pearl millet (*Pennisetum glaucum*) and finger millet (*Eleusine coracana*) for nutritional values as it contains high amounts of calcium (Gopala et al. 1989). After harvesting, the millet is used and husks are disposed of as agricultural waste which can be used as a source of cellulose.

To date few or no known works, on the optimization of the extraction of cellulose nanocrystals from finger millet husk using response surface methodology. The response surface methodology is employed to analyze the impact of process parameters and to predict the optimum condition at a minimized number of experiments. Optimization and studying the effect of process variables can be done using 3-level factorials, central composite design, hybrid, pentagonal, hexagonal, D-optimal, distance-based, and box Behnken (Zolgharnein et al. 2017).

In this study, the Box Behnken method in response surface methodology tool was used to determine the optimum conditions for the extraction of cellulose nanocrystals from millet husk. The selection of the design method was due to its capability which allows multiple responses. The individual numerical factor is varied over three levels and has fewer runs associated with the three-level factorials (Montgomery, 2005). This method does not require several central points since the points on the surface are closer towards the midpoint. The effects of process variables namely; homogenization speed, acid concentration, and acid to cellulose ratio on the yield and swelling of CNCs were investigated and optimized numerically. Analysis of variance (ANOVA) was also used as a statistical and diagnostic checking test tool. Additionally, cellulose and cellulose nanocrystal was characterized using X-ray Diffraction (XRD), Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA).

2. Materials And Methods

2.1 Materials

Millet husks residue used were obtained from a millet processing farm in Kenya. Sulfuric acid, sodium chlorite, sodium hydroxide, acetic acid, ethanol, and dialysis bag were supplied by Sigma Aldrich and Merck Chemical South Africa and were of analytical grade.

2.2. Production of cellulose from millet husk waste

The millet husk waste was washed, air-dried, milled, and sieved with a 45 mesh sieve. The oil was removed from the ground husk by solvent extraction with ethanol at 65°C for 6 hours. The unextracted sample was dried in an oven at 65°C for 15 hours and was stored in a tight polythene bag. 500 mL of aqueous sodium hydroxide (7.0%) was mixed with 50g of the sample. The mixture was agitated for 60 minutes at 25°C. The pretreated sample was filtered at 25°C before being repeatedly rinsed with 90% ethanol to remove wax and oil. After that, the sample was dried in an oven for 18 hours at 65°C. The sample was further mixed with 200 mL deionized water, 1.5g sodium chlorite, and 25mL acetic acid. The mixture was stirred for 3 hours at 70°C. The residue was rinsed with a mixture of distilled water and ethanol. The final sample was dried in an oven at 65°C for 20 hours. The cellulose obtained was used to produce cellulose nanocrystals.

2.3 Cellulose nanocrystals extraction

The acidic hydrolysis technique by (Priscila et al. 2019) was used to produce cellulose nanocrystals from cellulose with 65 wt % sulfuric acid used. Cellulose was mixed fully with the acid to cellulose ratio (1:15, 1:20, 1:25) using a homogenizer at speeds of (4000, 6000, 8000 rpm) for 10 min at 50 °C. After that, the suspension formed was diluted five times with deionized water to discontinue the hydrolysis process. The sample was further centrifuged for 15 minutes at 10000 rpm. The suspension that was left was further centrifuged to get rid of the excess sulphuric acid and the supernatant was disposed of. The suspension was placed in a dialysis bag and diluted with distilled water repeatedly to attain a pH of 7. The washed sample was homogenized in an ultrasonic set up for 15 min. The mixture was dried in a drier for 72 hours. To stop the microorganism contamination a drop of chloroform was added and lastly, the cellulose nanocrystal powder was preserved in a tight impenetrable vessel.

2.4 Physical and chemical properties of cellulose nanocrystals

2.4.1 Yield of cellulose nanocrystals

The CNCs yield was calculated using the technique proposed by (Hemmati et al. 2018). The samples were carefully measured using a precise digital balance. The measurement was done in triplicates the average and standard deviation was recorded. Eq. (1) was used to determine the yield of CNCs.

$$\text{Yield (\%)} = \frac{m_1 - m_2}{m_3} \times 100 \quad (1)$$

Where m_1 (g) is the weight of cellulose nanocrystals with the vial, m_2 (g) is the weight of the vial, and m_3 (g) is the weight of cellulose used.

2.4.2 Cellulose nanocrystals swelling capacity

The swelling capacity of CNCs was determined following the technique recommended by (Zou et al., 2018). Firstly, 2g of CNCs sample was weighed and placed in a conical flask. Then, 20 mL of distilled water was poured into the conical flask. The volume of the sample was measured after being stored for 24h at controlled room temperature. The swelling capacity was determined using Eq. (2).

$$SWC (mg/L)= \frac{V_2-V_1}{m} \times 100 \text{ (2)}$$

Where m (g) is the weight of the cellulose nanocrystals, V_1 (mL) is the volume initial of the CNCs, and V_2 (mL) is the volume of the CNCs together with the absorbed water.

2.5 Experimental design and optimization

2.5.1 RSM-Box Behnken experimental design

The evaluation of the linear, cubic, and quadratic effects on the yield and the swelling capacity of CNCs was done using the Box Behnken design in RSM. The choice of this design technique was to permit multiple responses and its capability to use three levels of factorials. Each numerical factorial is varied over three levels and has fewer runs compared to the three-level factorials (Montgomery, 2005). Three process variables were studied namely: Homogenization speed(A); acid concentration (B) and acid to cellulose ratio (C). The series of variables using coded values are shown in Table 1. The Box Behnken set of experiments conducted and the results of this study are shown in Table 2.

Table 1
Range of factors and their levels used in the Box Behnken design.

Variable	Coded symbol	Coded level		
		-1	0	+ 1
Homogenization speed(rpm)	A	4000	6000	8000
Acid concentration (wt %)	B	55	62.5	70
Acid to cellulose ratio (wt %)	C	15	20	25

Table 2
Box Behnken design and results for yield and swelling capacity of CNCs

Run	A: Homogenization speed (rpm)	B: Acid concentration (%)	C: Acid to cellulose ratio	Yield (%)	Swelling (%)
1	6000	62.50	20.00	87 ± 1.8	2.6 ± 2.9
2	4000	55.00	20.00	72 ± 2.3	3.7 ± 1.5
3	8000	62.50	15.00	85 ± 1.1	2.7 ± 3.8
4	6000	55.00	25.00	78 ± 1.2	3 ± 1.8
5	6000	55.00	15.00	80 ± 1.8	3.1 ± 2.6
6	8000	70.00	20.00	88 ± 3.2	2.8 ± 3.4
7	6000	62.50	20.00	92 ± 2.5	2.6 ± 3.6
8	4000	62.50	15.00	83 ± 2.7	2.5 ± 1.6
9	6000	70.00	15.00	80 ± 1.4	2.1 ± 3.2
10	6000	62.50	20.00	92 ± 2.1	2.57 ± 4.1
11	4000	70.00	20.00	77 ± 1.7	2.6 ± 2.3
12	6000	62.50	20.00	92 ± 2.5	2.59 ± 3.5
13	8000	55.00	20.00	87 ± 2.3	3.9 ± 1.4
14	6000	62.50	20.00	92 ± 1.9	2.6 ± 3.3
15	6000	70.00	25.00	77 ± 1.6	2.4 ± 2.2
16	8000	62.50	25.00	92 ± 1.2	2.8 ± 4.2
17	4000	62.50	25.00	87 ± 3.1	2.7 ± 3.9

The mathematical correlation amongst the independent variables and dependent variable in the response is explained by the second-order polynomial using Eq. (3).

$$Y = \gamma_0 + \gamma_a A + \gamma_b B + \gamma_c C + \gamma_{aa} A^2 + \gamma_{bb} B^2 + \gamma_{cc} C^2 + \gamma_{ab} AB + \gamma_{ac} AC + \gamma_{bc} BC \quad (3)$$

Where Y is the predicted response, γ_0 is the model constant, A, B, and C are independent variables, γ_a , γ_b and γ_c are linear coefficients and γ_{ab} , γ_{ac} and γ_{bc} are cross-product coefficients, and γ_{aa} , γ_{bb} and γ_{cc} are the quadratic coefficients.

2.5.2 Model fitting, statistical analysis, and numerical optimization

To fit experimental data to the second-order mathematical polynomial regression model, a design expert (11) software was used as a regression analyzing tool. The statistical importance evaluation of the model was determined using ANOVA and optimization was done numerically using the design expert software.

2.6 Characterization of cellulose and cellulose nanocrystals from millet husk

2.6.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy analysis of samples was performed using a VARIAN 7000 spectrometer. For each spectrum, 15 scans were accumulated over a resolution of 4 cm^{-1} and a range of $500\text{--}4500 \text{ cm}^{-1}$.

2.6.2 Scanning electron microscopy (SEM)

Scanning electron micrograph of samples was done using a Philips XL 30FEG scanning electron microscope. All samples were coated with platinum using the sputtering technique.

2.6.3 X-Ray diffraction (XRD)

X-ray diffraction of samples was carried out using Cu $\text{K}\alpha$ radiation source in a Phillips X'pert Model 0993. The diffraction intensity was recorded between 5 and 90° (2θ angle range) with a scanning speed of 0.4°C per min. The relative crystallinity index of the model was calculated by following Eq. (4) (Yalç et al. 2019).

$$\text{CI (\%)} = \frac{I_{02} - I_{an}}{I_{02}} \times 100 \quad (4)$$

I_{02} is the maximum diffraction intensity of the plane and I_{an} represents the diffraction intensity of the amorphous part.

2.6.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the sample was investigated using thermogravimetric analyzer NETZSCH5 209F3 over a heat range of 50 to 700°C at the heating rate of 10°C/min under nitrogen gas.

3. Results And Discussion

3.1 The development of quadratic for predicting yield and swelling capacity of CNCs

The insignificant terms were eliminated using the Fischer's test in design expert software and the resulting final equation for predicting the yield and swelling capacity of CNCs are shown in Eq. (7) and Eq. (8) respectively.

$$\text{Yield (\%)} = 91.48 + 4.04A + 0.59B + 0.83C - 0.90AB + 0.81AC - 0.19BC - 1.22A^2 - 9.31B^2 - 3.54C^2 \quad (7)$$

$$\text{SWC (\%)} = 2.58 + 0.09A - 0.46B + 0.06C + 0.05AB - 0.01AC + 0.19BC + 0.33A^2 + 0.32B^2 - 0.25C^2 \quad (8)$$

The negative and positive signs in the quadratic model to predict the yield and swelling capacity of CNCs expresses the antagonist effect and synergic effect in the model.

The regression coefficient (R^2) values of the obtained models are 0.989 for the yield and 0.979 for the swelling capacity of CNCs. This means that 98.9 and 97.9% of the experimental data can be explained by the model for the yield and swelling capacity of CNCs as shown in Fig. 1.

3.2 ANOVA for regression results for yield and swelling capacity of CNCs

Table 3 and Table 4 show the ANOVA for the regression model for predicting the yield and swelling of CNCs respectively. The quadratic model equations show that $F = 672.80$ and $F = 413.55$ for the yield and swelling capacity of CNCs respectively with $P \leq 0.0001$ suggest that the models are significant in predicting yield and the swelling capacity. As shown in Table 3 from the ANOVA results for predicting the yield of CNCs it was observed that the homogenization speed and acid to cellulose ratio individual terms are significant terms in the model while the acid concentration term is insignificant. In the case, ANOVA results shown in Table 4 for predicting the swelling capacity of CNCs in all individual terms are significant in the model. The interaction terms are insignificant while all quadratic terms are significant in the model for predicting the yield and swelling capacity of CNCs.

Table 3

ANOVA for regression model equation for the yield of CNCs when insignificant terms are removed.

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Significance
Model	594.12	9	66.01	672.80	< 0.0001	significant
A-Homogenization speed	130.49	1	130.49	1329.95	< 0.0001	
B-Acid concentration	2.87	1	2.87	29.23	0.001	
C-Acid to cellulose ratio	5.51	1	5.51	56.17	0.0001	
AB	3.26	1	3.26	33.21	0.0007	
AC	2.66	1	2.66	27.08	0.0012	
BC	0.14	1	0.14	1.47	0.0264	
A ²	6.31	1	6.31	64.26	< 0.0001	
B ²	364.85	1	364.85	3718.53	< 0.0001	
C ²	52.65	1	52.65	536.63	< 0.0001	
Residual	0.68	7	0.098			

Table 4
Results of ANOVA for regression model for the swelling capacity of CNCS when insignificant terms are removed.

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Significance
Model	3.05	9	0.3394	413.55	< 0.0001	significant
A-Homogenization speed	0.0648	1	0.0648	78.96	< 0.0001	
B-Acid concentration	1.76	1	1.76	2141.81	< 0.0001	
C-Acid to ratio	0.0378	1	0.0378	46.07	0.0003	
AB	0.0001	1	0.0001	0.1218	0.7373	
AC	0.0004	1	0.0004	0.4874	0.5076	
BC	0.038	1	0.038	46.33	0.0003	
A ²	0.4704	1	0.4704	573.17	< 0.0001	
B ²	0.4359	1	0.4359	531.11	< 0.0001	
C ²	0.27	1	0.27	329.04	< 0.0001	
Residual	0.0057	7	0.0008			

3.3 The effect of process variables on the yield and swelling capacity of CNCs from cellulose.

3.3.1 Effects of homogenization speed and acid concentration on the yield of CNCs

Figure 2 shows the effect of homogenization speed and acid concentration on the yield of CNCs; the acid to cellulose mass ratio is held constant at 20 wt %. At high acid concentration, the yield of CNCs is much higher than at low acid concentration. This may be attributed to the fact that at low acid concentration the acid can't access and attack the amorphous regions of the cellulose. At a high acid concentration, as time and homogenization speed is increased, the glucose may be generated as a result of the degradation of the cellulose and hence a reduction in the number of cellulose nanocrystals produced.

As the homogenization speed is increased the yield of CNCs increases this is because homogenization speed increases the chances of which the cellulose particles are distributed throughout the sulphuric acid.

Another explanation could be that as homogenization speed is increased there is more collision between the cellulose and the sulphuric acids which breaks down the glycosidic bond between cellulosic chains which results in reduced amorphous chains and more crystalline structure.

3.3.2 Effects of acid to cellulose ratio and acid concentration on the yield of CNCs

Figure 3, shows the effect of acid to cellulose ratio and acid concentration on the yield of CNCs, the homogenization speed is held constant at 6000 rpm. At higher acid, to cellulose mass ratio the yield of CNCs is higher than at low acid to cellulose ratio. This is because there is more cellulose to be attacked per unit volume of acid and hence more CNCs. As the acid concentration is increased the yield increases to a maximum level and then decreases. The main reason could be as the acid concentration is increased the crystalline part of the cellulose decomposes resulting in less yield of CNCs and also the glucosidic bond between cellulosic chains breaks down, resulting in shorter chains with irregular structure (Henschen et al. 2019; Souza et al. 2017).

3.3.3 Effects of homogenization speed and acid concentration on the swelling capacity of CNCs

Figure 4, shows the effect of homogenization speed and acid concentration on the swelling capacity of CNCs; the acid to cellulose ratio is held constant at 20 wt %. At high acid concentrations, the swelling capacity of CNCs is much lower than at low acid concentrations. The explanation could be the generation of glucose at the beginning process as a result of degradation which reduces the amount of CNCs and hence lowering the swelling capacity at high acid concentration. As the homogenization speed is increased the swelling capacity decreases and then increases (Minimax behavior). The reason could be there is no enough time to allow the sulphuric acid to diffuse into the chains of the cellulose. As the homogenization speed is increased, the breaking of the cellulose configuration occurs and their conversion to nanocellulose, causes extreme modifications to occur in the physicochemical attributes increasing the swelling capacity (Lei et al. 2019; Wang et al. 2015).

3.3.4 Effects of acid to cellulose ratio and acid concentration on the swelling of CNCs

Figure 5, shows the effect of acid to cellulose ratio and acid concentration on the swelling of CNCs; the homogenization speed is held constant at 6000 rpm. At low acid, to cellulose ratio, the swelling capacity is lower than at high acid to cellulose ratio. This is because there is more cellulose to be attacked per unit volume of acid and hence swelling capacity of CNCs increases. As the acid concentration is increased the swelling capacity decreases since the degradation starts with the most accessible region of the cellulose fiber and this reduces the end groups and the crystalline regions drastically and hence the swelling capacity drops (Lei et al. 2019; Chen et al. 2012).

3.5 Individual influence of process variables on the yield and swelling capacity of CNCs from cellulose.

As shown in Fig. 6, the perturbation plot shows the effect of process variable on the the yield and swelling capacity of CNCs from cellulose. Influence of one factor was evaluated and plotted alongside the yield and the swelling capacity while the other variables were retained at a constant level. As shown in Fig. 6A, the homogenization speed and acid to cellulose ratio posses a great influence on the yield of CNCs from cellulose in comparison to the acid concentration. As shown in Fig. 6B, for the swelling capacity of CNCs, the homogenization speed and acid concentration posses a great influence while the acid to cellulose ratio shows the least influence.

From the perturbation plot, the yield and swelling capacity of CNCs from cellulose decreases as the acid concentration and acid to cellulose ratio is increased and increases with a increase of the homogenization speed. The result is in excellent agreement with the result acquired from the analysis of variance (ANOVA).

3.5 Numerical optimizations

The numerical optimization technique in the design expert software was used due to the maximum and minimum detected in the three-dimensional response surfaces. The objective function which is the yield and swelling capacity of CNCs was set at a maximum approach and all the other process variables namely homogenization speed, acid concentration, and acid to cellulose ratio were fixed at the range for optimization. the numerical optimization analysis results showed that the maximum yield of CNCs from cellulose was 93.12 % and was obtained at homogenization speed, acid concentration, and acid to cellulose ratio of 7464.0 rpm, 63.40 wt %, and 18.83 wt % respectively. While the maximum swelling capacity of 2.81 % was obtained at homogenization speed, acid concentration, and acid to cellulose ratio of 80000 rpm, 62.5 wt %, and 25 wt % respectively.

For this optimization, the desirability of 0.986 and 0.996 was obtained for yield and swelling capacity of CNCs respectively, which indicates that the response is inside the desirable limits and this suggests that the optimized operational conditions that can be trusted in achieving the maximum yield and swelling capacity of CNCs provided by the model.

4. Characterization Results

4.1 Fourier-transform infrared spectroscopy (FTIR)Analysis

FTIR functional groups for cellulose and cellulose nanocrystals (CNC) are depicted in Fig. 7. The wideband between $3100\text{--}3600\text{ cm}^{-1}$ is assigned to the vibration O-H group and it is attributed to hydrogen bonds due to molecular interactions in cellulose. Also, the bands at 2880 cm^{-1} and 2780 cm^{-1} are corresponding to the stretching vibration C-H group. The band at 1650 cm^{-1} present for CNCs is assigned to the O-H group. Conversely, this band was not existing in the original cellulose (Hemmati et al. 2018). This factor may be related to the sulfate groups existing on the external surface of the cellulose nanocrystals in the aqueous phase of CNCs, which will increase the hydrophilicity of the CNCs. The band at 1600 cm^{-1} is assigned to C = C, which represents the magnetism of the aromatic cycle in lignin

formation in cellulose, it was degraded by acid hydrolysis in the CNCs. The band at 1430 cm^{-1} is linked to the OH and C-H group available in the cellulose, but the group is drastically reduced in the CNCs due to the hydrolysis process (Meng et al. 2019). The band at 1320 cm^{-1} is assigned to the bending vibration of CH₂. Other band includes 1030 cm^{-1} for morphological modification in C-O and 890 cm^{-1} which shows the common configuration of cellulose with the β glycoside bonds in the glucose ring.

4.2 X-ray diffraction (XRD) pattern

Figure 8. elucidates the XRD analysis of cellulose and CNCs. Three common peaks were observed for cellulose and CNCs at 2θ angles of 16.6° , 27.4° , and 40.0° regions. The crystalline index of cellulose was 48% based on Fig. 8. The alkali hydrolysis and lignin in cellulose are removed by concentrated sulfuric acid, the amorphous region in the cellulose configuration is detached and the crystallinity index is improved (Oyewo et al. 2019). After acid hydrolysis, the crystallinity index was around 70%. The % degree of crystallinity is influenced by the source of cellulose, the period of CNCs purification, and the process conditions of hydrolysis. There is a straight connection between the degree of crystallinity and the hardness of the cellulose. The harder the cellulose, the higher the crystallinity index (Ishak et al. 2019). In other studies, related to this work, the crystallinity index of peanut shells and pine bark are 36.7° and 55° respectively, which is similar to the crystallinity index measured in this study.

4.3 Thermogravimetric analysis (TGA)

The thermal stability of cellulose and cellulose nanocrystals (CNCs) is presented in Fig. 9. As it can be depicted in the graph the temperature decreased slightly between 60 and 100°C for both cellulose and CNCs graphs, indicating the loss of water due to evaporation. The weight loss of both samples at this stage is less than 6%, and for cellulose, there was a further loss at the temperature range between 260 to 400°C , this is associated with the decomposition of alpha-cellulose and lignin. At this phase, the mass loss of 85% of the cellulose occurs. This may be linked to the destruction of chains in cellulose and due to the disintegration of glycosyl cellulose chains and decarboxylation (Hemmati et al. 2018). At temperatures above 400°C , the mass loss is assigned to oxidation and the formation of residual ash in low-weight gases. At this phase, the residual content is less than 10% at 600°C .

The CNCs showed a dissimilar thermal stability trend as compared to cellulose. The main mass loss of the CNCs occurred at the temperature range of between 240 to 380°C and the sample lost 79% of its weight. For the CNCs, degradation occurred over a wider temperature range as compared to cellulose. The large surface area of CNCs can play a key role in decreasing the thermal stability because in the CNCs the contact surface advances the heat transfer. Furthermore, through acid hydrolysis with sulfuric acid, both amorphous and crystalline structures decompose, this fact makes the arrangements within the CNCs are more sensitive to heat (Leszczy et al. 2018).

4.4 Scanning electron microscopy (SEM) analysis

Figure 10, shows the SEM images of cellulose and cellulose nanocrystals (CNCs). The SEM images depict that the alpha-cellulose fibers were relatively easy to see and more regular surfaces were observed after the elimination of the non-cellulosic components. On the other hand, the cellulose nanocrystals (CNCs) cover the surface in the form of short fibers and fine fibers, this is probably because sulfuric acid penetrated the amorphous region of cellulose, causing the hydrolysis and degradation of glucopyranose linkage. The actual structure of the cellulose nanocrystals is visible, probably due to the drying process, the presence of nanocrystals cluster around ice crystals is the result of the large number of hydrogen bonds formed between the surfaces.

5. Conclusion

This study shows that it is possible to extract cellulose nanocrystals (CNCs) from cellulose using millet husk residue waste. A Box Behnken design was used to investigate and optimize the effect of homogenization speed, acid concentration, and acid to cellulose ratio on the yield and swelling capacity of CNCs. Results show the yield and swelling capacity of CNCs from cellulose decreases as the acid concentration and acid to cellulose ratio is increased and increases with an increase in homogenization speed. The maximum yield of CNCs of 93.12 wt % was obtained at homogenization speed, acid concentration, and acid to cellulose ratio of 7464.0 rpm, 63.40 wt %, and 18.83 wt % respectively. The optimum swelling capacity of 2.81 % was obtained at homogenization speed, acid concentration, and acid to cellulose ratio of 8000 rpm, 62.5 wt %, and 25 wt % respectively. A mathematical model was obtained to predict the yield and the swelling capacity of cellulose nanocrystals with R^2 of the value of 98.9 % and 97.9% respectively. The cellulose and nano-cellulose obtained were characterized using transform infrared microscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The TGA showed that the thermal stability of cellulose was higher than that of CNCs, FTIR results showed function group of CNCs and cellulose were similar, SEM image of CNCs is porous and displayed narrow particle size and needle-like morphology as compared to cellulose and XRD pattern presented an increase in the intensity of CNCs.

6. Abbreviations

CNCs

Cellulose nanocrystals; FTIR:Fourier transform infrared; SEM:Scanning electron microscope; X-ray diffraction (XRD); Thermogravimetric analysis (TGA).

7. Declarations

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Authors' contributions

MB—conceptualization, data collection, investigation, and writing the original draft. HR—supervision, review, validation, and editing.

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Availability of data and materials

All data are available in this manuscript.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Figures

Figure 1

A plot between the predicted and experimental values for yield (A) and (B) for swelling capacity of CNCs.

Figure 2

Effect of homogenization speed and acid concentration on the yield of CNCs, (A) response surface and (B) two-dimension plot with acid concentration held at (-) 55 wt % and (+) 70 wt %.

Figure 3

Effect of acid to cellulose ratio and acid concentration on the yield of CNCs, (A) response surface and (B) two-dimension plot with acid to cellulose ratio (wt %) held at (-) 15 wt % and (+) 20 wt %.

Figure 4

Effect of homogenization speed and acid concentration on the swelling capacity of CNCs, (A) response surface and (B) two-dimension plot with acid concentration held at (-) 55 wt % and (+) 70 wt %.

Figure 5

Effect of acid to cellulose ratio and acid concentration on the yield of CNCs, (a) response surface and (b) two-dimension plot with acid to cellulose mass ratio held at (-) 15 wt % and (+) 20 wt %

Figure 6

Perturbation plots showing the effects of (A) homogenization speed, (B) acid concentration, and (C) cellulose to acid ratio on the yield and swelling capacity

Figure 7

FTIR transmittance of cellulose and cellulose nanocrystals (CNCs)

Figure 8

XRD patterns of cellulose and cellulose nanocrystals (CNCs)

Figure 9

TGA graph for cellulose and cellulose nanocrystals CNCs

Figure 10

SEM image of cellulose (A) and cellulose nanocrystals (CNCs) (B)

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