

Preparation of Dicarboxyl Cellulose Nanocrystals from Agricultural Wastes by Sequential Periodate-Chlorite Oxidation

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Abstract: Agricultural waste straw is the renewable resource with the highest annual yield in the world. In value-added applications of agricultural waste, dicarboxyl cellulose nanocrystals (DCCs) are prepared from rice, wheat, and corn straw by sequential periodate-chlorite oxidation. In this study, DCCs from rice, wheat, and corn straw were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectrometer, X-ray diffractometer (XRD), and thermal gravimetric analysis (TGA). The carboxyl content of the DCCs was also investigated. XRD results show that the crystallinity index decreased after sequential periodate-chlorite oxidation; however, the cellulose I structure was maintained. TEM results show that rod-shaped DCCs with an average length and width of 287.0 nm and 9.9 nm, respectively, were successfully prepared by sequential periodate-chlorite oxidation. The carboxyl content of the DCCs was around 3.9 mmol/g, and not affected by the type of straw. Experiments to study the removal of copper ions in aqueous medium were performed with the prepared DCCs. The adsorption capacities of copper ions were 131, 162, and 144 mg/g for DCCs prepared from rice, wheat, and corn straws, respectively. The results show that DCCs prepared from rice, wheat, and corn straws by sequential periodatechlorite oxidation have potential for the removal of copper ions from aqueous medium.

Keywords: Agricultural waste; dicarboxyl cellulose nanocrystals; sequential periodate-chlorite oxidation; copper ion removal

1 Introduction

Agricultural waste straw is one of the most abundant lignocellulosic residues in the world, with an annual yield of 5.1 billion tons [1]. However, there is scope to improve the use of waste straw, with a significant amount being used as fuel for field burning [2]. The cultivated area of Heilongjiang Province in China is 15.9 million hectares, and the annual straw yield is approximately 130 million tons, accounting for about 1/8th of the total straw yield in China [1,3]. Therefore, a simple and efficient value-adding method for treating agricultural waste is of significant interest.

Cellulose, the main component of straw, is a linear polymer compound composed of a D-glucopyranose ring connected by β -1,4-glucosidic bonds in a C1 chair conformation. Nanocelluloses, prepared through the



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use of physical, chemical, or biological technologies have a size between 1 and 100 nm in at least one dimension and are a renewable, biodegradable, biocompatible, and environmentally conscious material. Nanocelluloses are promising due to their intrinsic properties, renewability, and abundance. Nanocelluloses are often classified into three main groups: cellulose nanofibrils (CNFs, also known as nanofibrillated cellulose), cellulose nanocrystals (CNCs, also referred to nanocrystalline cellulose or cellulose nanowhiskers), and bacterial nanocellulose (BNC, also known as microbial nanocellulose) [4].

CNFs can be prepared by homogenization [5], refining [6], grinding [7], and ultrasonication [8,9]. When exposed to high shear forces in a low pressure environment with disordered flow and particle collisions, the cellulosic fibers can be cut and fibrillated into nanofibers; however, the mechanical methods for preparing CNFs are prone to clogging and high energy consumption, with energy consumption reaching 4.4 kWh/kg, and the size of the CNFs relatively large, with the particle size distribution being non-homogenous [10,11].

The combination of chemical pretreatment and mechanical methods is an emerging research direction in nanocellulose preparation [12]. Isogai et al. used the TEMPO/NaBr/NaClO methodology to selectively oxidize cellulose under alkaline conditions. This system oxidizes the C-6 hydroxyl groups to carboxyl groups on the outer layer of the cellulose, and the carboxyl group content can reach 1.7 mmol/g [13,14]. Due to this carboxyl group the repulsive force between cellulose chains increases, and the cellulose filaments are released by mechanical treatment and CNFs with a length of several hundred nanometers and a width of 3–4 nm are obtained [13,15]. Hirota et al. used the TEMPO/NaClO₂/NaClO system to oxidize cellulose under neutral or slightly acidic conditions, followed by mechanical treatment to prepare CNFs with a high carboxyl content [16]. However, this method cannot be performed at room temperature, and the reaction time is 72 h. The thermal stability of the prepared CNFs is poor and the system consumes significant mechanical energy.

Acid hydrolysis is a relatively mature method for preparing CNCs [17]. The strong acid destroys the hydrogen bonds and hydrolyzes amorphous regions in the cellulose fibers. Different inorganic acid treatments impart specific functional groups on the surface of the nanoparticles and affect colloidal stability. CNCs produced by hydrochloric acid show poor colloidal stability [18]. CNCs prepared by sulfuric acid introduce negatively charged sulfate ester groups on the CNC surface, causing electrostatic repulsion, which results in highly stable colloidal dispersions [19]. Currently, acid hydrolysis requires a high-volume of inorganic acid and has specific requirements for reaction equipment, making large-scale production of nanocellulose using this methodology environmentally unsustainable [20].

There are key challenges in the efficient preparation of nanocellulose. Firstly, the raw materials are mainly wood, which consume valuable environmental resources. To improve feasibility, the source of cellulose should be converted from wood to agricultural waste [21]. Secondly, the hydroxyl groups at the 2, 3, and 6 positions on the surface of the cellulose chain constitute a large number of intermolecular and intramolecular hydrogen bonds, which limits the application of cellulose. Functional modification of the hydroxyl groups expands the possible applications of the material. More reactive sites on the side chains of cellulose can be realized by introducing active groups such as aldehyde, carboxyl, and amino groups to substitute with the hydroxyl groups. This chemically modified nanocellulose can be incorporated into polymer matrices to improve physical properties, including heavy metal ion adsorption and oxygen blocking [22–24]. Thirdly, although straw nanocellulose can be prepared through different methods, the properties of the obtained nanocellulose are affected by the type of raw material, as there are many types of agricultural waste straw with varied composition and structure. There is no universal method for preparing functional nanocellulose using agricultural waste straw as the raw material [25].

In this study, the sequential periodate-chlorite oxidation method was used to prepare dicarboxyl cellulose nanocrystals (DCCs) from rice, wheat, and corn straw for the first time. The results show that

the carboxyl content in DCCs is not affected by the raw material, and that the carboxyl content is related to experimental conditions. The adsorption capacity of copper ions is more than 160 mg/g for DCCs prepared from agricultural waste straw. The results show that the DCCs prepared from agricultural waste straw by sequential periodate-chlorite oxidation have potential in the removal of copper ions from aqueous medium. This study provides a new direction for the future commercial production of nanocellulose as well as a novel method for the treatment of agricultural waste.

2 Materials and Methods

2.1 Materials

Rice, wheat, and corn straw were supplied by Xiangyang Farm of Northeast Agricultural University. All chemicals are analytical grade and used without any further purification. Sodium periodate (NaIO₄), hydroxylamine hydrochloride (NH₂OH·HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium chlorite (NaCl) and sodium chlorite (NaClO₂) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl) and acetic acid (CH₃COOH) were purchased from Tianjin Damao Chemical Reagent Factory. Anhydrous ethanol, ethylene glycol, isopropanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd., (Tianjin China). Hydrogen peroxide (H₂O₂) with a concentration of 30 w/v% was purchased from Tianjin Yongda Chemical Reagent Co., Ltd., and used as received. Deionized water was used throughout the experiments.

2.2 Methods

2.2.1 Purified Cellulose

Rice, wheat, and corn straw were mechanically ground to 100 mesh with a knife mill (Wiley Mill E3300, Eberbach Corporation) prior to chemical treatment. Cellulose was extracted from straw by bleaching and alkali treatment. First, the bleaching treatment was performed for 2 h at room temperature with a 1.5 w/v% sodium chlorite (NaClO₂) solution (adjusted to a pH of 4 with acetic acid) at a fiber to liquor ratio of 1:50. Next, the obtained fibers were dispersed into 500 mL of 2.5% potassium hydroxide (KOH) solution, and treated for 2 h at 90°C. Then, the obtained fibers were dispersed into 500 mL of 5% potassium hydroxide (KOH) solution, and treated for 2 h at 90°C. The obtained fibers were washed by filtration with deionized water. Then, bleaching was performed for 6 h at room temperature with sodium chlorite (NaClO₂) solution (adjusted to a pH of 1:50. The recovered fibers were filtered with deionized water until a neutral pH was reached. Finally, the purified cellulose was oven-dried to a constant mass and weighed [26]. The yield of purified cellulose was expressed as the mass percentage of purified cellulose to straw.

2.2.2 Periodate Oxidation

Periodate oxidation of purified cellulose has been previously reported, with this work featuring changes to obtain dialdehyde cellulose (DAC) [27]. Specifically, 4 g of purified cellulose was soaked in 266 mL of water for 24 h. Next 5.33 g NaIO₄ and 15.6 g NaCl were dissolved in water, and the purified cellulose was added to the solution. The reaction beaker was wrapped with aluminum foil to prevent light irradiation. The oxidation reaction was performed at room temperature whilst being stirred for 24 h. Ethylene glycol was added to the mixture to end the reaction by quenching of the residual periodate. The oxidized cellulose was thoroughly washed by centrifuging in deionized water (1500 g for 5 min) to remove ethylene glycol and formaldehyde until the conductivity of the supernatant after centrifugation is less than 30 μ S/cm. The final products were dried in a freeze-dryer (FD-1A-50, Beijing Bo Yikang Experimental Instrument Co., Ltd.). The yield of DAC was expressed as the mass percentage of DAC to purified cellulose.

2.2.3 Chlorite Oxidation

One gram of DAC was suspended in water (50 mL, including the moisture content of the DAC), 2.93 g NaCl, NaClO₂ and H_2O_2 (with a molarity twice that of the aldehyde content of the DAC) were added to this

mixture. The mixture was stirred for 24 h at room temperature and the pH was maintained at 5.0 by adding 0.5 M NaOH [28]. After the reaction, the oxidized cellulose was washed by centrifuging with deionized water at 8500 g for 5 min (TG5B, Changsha Yingtai Instrument Co., Ltd.). Then washed with 0.5 M hydrochloric acid and absolute ethanol three times, and finally washed with deionized water. After centrifugation, the supernatant conductivity is less than 30 μ S/cm. The final product is dried with a vacuum freeze dryer (FD-1A-50, Beijing Bo Yikang Experimental Instrument Co., Ltd.) resulting in DCCs being obtained. After drying, the mass of the DCCs was weighed and recorded, and stored in a refrigerator at 4°C. The yield of DCCs was expressed as the mass percentage of DCCs to DAC.

2.2.4 Aldehyde Content

The aldehyde content of the DACs produced by the periodate oxidation reaction was determined by hydroxylamine hydrochloride (NH₂OH·HCl) titration [29]. First, a suspension of 0.1 g of DAC with 10 ml of water was mixed with 20 mL of isopropanol so that the final ratio of isopropanol/water was 2:1 (ml:ml) and the mixture was stirred for 30 min. Next, the concentrated HCl was added dropwise to adjust the pH of the mixture to 2–3, then the pH was adjusted to 3.5 with 0.1 M NaOH. Then, 10 mL of a 10% NH₂OH·HCl solution was added to the mixture and allowed to react for 30 min. Finally, the solution was titrated with a 0.5 mol/L NaOH solution until the pH reached 3.5. The aldehyde content was calculated with the following equation:

$$A_{ald} = \frac{V_{\text{NaOH}} \times \text{N}}{W_{\text{CEL}}} \tag{1}$$

where A_{ald} is the content of aldehyde group consumed in titration (mmol/g cellulose); V_{NaOH} , the volume of NaOH (mL); N, the NaOH equivalent concentration (0.5 mol/L) and W_{CEL} the weight of initially suspended DAC (g).

2.2.5 Carboxyl Content

First, 0.1 g of DCCs was dispersed in 100 mL of 0.5 M NaCl solution, stirred and mixed, and 5 ml of a 0.1 M HCl-0.5 M NaCl mixed solution slowly added and mixed. Next, a titration was performed with a mixture of 0.1 M NaOH-0.5 M NaCl whilst stirring. The potential change was recorded with an automatic potentiometric titrator (ZD-2, Shanghai LeiCi Magnetic Instrument Co., Ltd.,). The carboxyl content of the samples was determined from the conductivity curve. The molar mass concentration of the corresponding oxidized cellulose carboxyl group was calculated using Eq. (2), with three parallel experiments being performed [30]:

$$[\text{COO}^{-}] = \frac{\left(V_{\text{NaOH}(\text{added})} - V_{\text{HCL}}\right) \times M_{\text{NaOH}}}{W_{\text{CEL}}}$$
(2)

where $[COO^-] = \text{carboxyl content (mmol/g)}$; V_{NaOH} (added) = the volume of NaOH at the inflection point (ml); V_{HCl} = the volume of HCl added to the 0.1 M HCl-0.5 M NaCl mixed solution (mL); M_{NaOH} = equivalent concentration of NaOH (mol/L) and W_{CEL} = starting mass of DCCs (g).

2.2.6 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) was performed to determine the effect of the regioselective oxidation process on the crystallinity and crystal structure of cellulose. XRD patterns were obtained using an X-ray diffractometer (D/max 2200, Rigaku, Japan) with Ni-filtered CuK α radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. Diffraction data was collected over the 5–40° 20 range, at a scanning rate of 0.7°/min. The relative crystallinity index (CrI) was determined using the Segal method with the following equation [31]:

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$
(3)

where *CrI* is the sample crystallinity index, %; I_{002} the maximum diffraction intensity at a diffraction angle of $22^{\circ}-23^{\circ}$; I_{am} , the minimum diffraction intensity at a diffraction angle of $18-20^{\circ}$. Here, I_{002} is the intensity of the 200-plane reflection, which is usually located around 22.6° ; I_{am} , the intensity at a diffraction angle of 18° , which corresponds to the minimum value in the diffraction pattern.

2.2.7 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna 560 instrument (Thermo Fisher, Waltham, MA, USA) fitted with a diamond attenuated-total-reflectance (ATR) attachment. Spectra was recorded in ATR mode over the 500–4000 cm⁻¹ range in absorbance mode, with 32 scans per spectrum at a resolution of 4 cm⁻¹. The background was subtracted prior to analysis.

2.2.8 Transmission Electron Microscopy (TEM)

The samples were observed with transmission electron microscopy (TEM) using a JEM-2100 transmission electron microscope (JEOL Ltd., Japan) at an accelerator voltage of 200 kV. A droplet of the diluted slurry was dropped on the carbon-coated electron microscopy grid and then negatively stained with 2 wt% phosphotungstic acid solution to enhance image contrast. The dimensions of the DCCs were determined from the TEM images using the Image J TEM-image-processing software.

2.2.9 Thermogravimetric Analysis (TGA)

The thermal stability of the purified cellulose, and DCC samples was tested by thermal gravimetric analysis (TGA) (SDTQ 600 (USA)) at a heating rate of 10 °C/min from 50°C to 800°C under a nitrogen atmosphere.

2.2.10 Adsorption of Copper Ions

Stock solutions of 10 g/L copper ion concentration were prepared by dissolving anhydrous copper chloride in deionized water. Freeze dried DCCs of 0.2 g was mixed with 100 mL copper ion solution and continuously stirred at $25 \pm 2^{\circ}$ C for 2 h. To avoid the formation of insoluble metal hydroxides, the pH of adsorption experiments was maintained at 6.0. Either 0.1 mol/L HCl or 0.1 mol/L NaOH solutions were used to adjust the pH values during the adsorption experiments. After centrifugation at 8500 g for 5 min, the copper ion concentration after adsorption was analyzed using a flame atomic absorption spectrometer (900 H, PerkinElmer). The adsorption capacity, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{4}$$

where C_0 (mg/L) is the initial copper ion concentration, C_e (mg/L) is the copper ion equilibrium concentration, V (L) is the volume of the copper ion solution and m (g) is the mass of adsorbent.

To investigate the reusability of DCCs, 0.2 g DCCs were used for adsorbing copper ions in 100 mL copper ion solutions with concentrations of 10 g/L. Then the DCCs adsorbed copper ions was centrifuged and desorbed with 50 mL of 0.5 M HCl at $25 \pm 2^{\circ}$ C for 30 min. The desorbed DCCs was reused for adsorption to evaluate its reusability, and the adsorption-desorption process was repeated 5 times.

3 Results and Discussion

3.1 XRD Analysis

X-ray diffraction was used to analyze the changes in the crystal structure and crystallinity of purified cellulose, and DCC samples. Fig. 1 shows that the crystal form of the purified cellulose, and DCCs remain intact, with the cellulose I structure retained. The CrI of purified cellulose from rice, wheat, and



Figure 1: XRD patterns of purified cellulose and DCCs. (a) R-CEL, (b) W-CEL, (c) C-CEL, (d) R-DCC, (e) W-DCC and (f) C-DCC

corn straw (R-CEL, W-CEL, and C-CEL) were 66.8%, 65.8%, and 61.3%, respectively (Tab. 1). The CrI of the DCCs prepared from rice, wheat, and corn straw (R-DCC, W-DCC, and C-DCC) were 44.5%, 54%, and 50.9%, respectively. These results are consistent with the results from Varma et al. [32] and Kim et al. [33]. This showed that the CrI of cellulose decreased as the degree of oxidation of periodate and chlorite increased. With the increased reaction time, the oxidant penetrates and diffuses inside the cellulose fiber molecular chain, from the amorphous region to the surface of the crystalline region, and then penetrates from the surface of the crystalline region [34]. Therefore, the crystallinity of cellulose decreased when the degree of oxidation increased.

	R-CEL	W-CEL	C-CEL	R-DAC	W-DAC	C-DAC	R-DCC	W-DCC	C-DCC
CrI (%)	66.8 %	65.8 %	61.3 %	44.6 %	54.0 %	51.2 %	44.5 %	54.0 %	50.9%
Length (nm)	_	_	_	_	_	_	294.7	431.9	135.0
Width (nm)	_	_	_	_	_	_	13.3	8.4	7.9
L/W (a.u)	_	_	_	_	_	_	22.2	51.4	17.1
Aldehyde (mmol/g)	_	_	_	3.12	3.34	3.87	0	0.01	0.01
Carboxyl (mmol/g)	_	_	_				3.77a	3.89a	4.03a
Yield (%)	31.3%	34.4%	38.5%	80.2%	81.9%	79.2%	51.9%	61.4%	57.2%

Table 1: Comparison of purified cellulose, DAC, and DCCs

The yields of R-CEL, W-CEL, and C-CEL are 31.3%, 34.4%, and 38.5%, respectively (Tab. 1). The yields of R-DAC, W-DAC, and C-DAC are 80.2%, 81.9%, and 79.2%, respectively. By calculation based on the ratio of DCCs to the mass of initial straw, the yields of R-DCC, W-DCC, and C-DCC are 13.0%, 17.3%, and 17.4%, respectively. These results are similar with the results from Jiang et al. [35]. They reported that the yields of nanocellulose materials prepared from rice straw by the mechanical, the TEMPO-mediated oxidation, and the sulfuric acid hydrolysis were 12.0%, 19.7%, and 16.9%, respectively.

3.2 FTIR Spectroscopy

Fourier transform infrared spectroscopy was used to evaluate structural changes that occurred in the cellulose following oxidation. Fig. 2 shows the FTIR spectra of cellulose, and DCC samples. The



Figure 2: FTIR spectroscopy of purified cellulose and DCCs R-CEL, (b) W-CEL, (c) C-CEL, (d) R-DCC, (e) W-DCC and (f) C-DCC

characteristic hydrogen-bonded O–H stretching peak of cellulose, centered at 3400 cm⁻¹, and that corresponding to sp3-hybridized C–H stretching, at 2900 cm⁻¹, are visible in the spectra of all samples. The C=O stretching vibration was observed at 1720 cm⁻¹. The sharp absorptions at 1027 cm⁻¹ are assigned to CH₂–O–CH₂ stretching, while the small peaks at 897 cm⁻¹ are due to the stretching of hemiacetal linkages. The small broad peak at approximately 1636 cm⁻¹ is due to the bending vibrations of residual water molecules in the cellulose and DCC samples [36,37].

The carboxylic groups within the DCCs exist as dimers, with the -O-H stretching vibration seen at 3400 cm⁻¹; due to the influence of hydrogen bonding, the absorption peak of C=O shifted to the low-frequency end to 1720 cm⁻¹, and the characteristic absorption peak of -OH in the dimer appeared at 890 cm⁻¹. These results show that the hydroxyl groups were successfully oxidized to carboxyl groups [38,39].

3.3 Carboxyl Content and Theoretical Carboxyl Content of DCCs

Tab. 1 shows the aldehyde and carboxyl content for DCC samples. The hydroxyl groups at the C2 and C3 of purified cellulose were selectively oxidized to aldehyde groups by sodium periodate. The amorphous region of cellulose is attacked first, then reacts at the surface of the crystalline region, and then penetrates from the surface of the crystalline region to inside the crystalline region. At the same time, periodate has a peeling effect on cellulose chains. For every 1 mmol/g increase in aldehyde content, a loop of filaments in the outer layer of the cellulose chain is peeled off, leaving a regular and orderly dialdehyde cellulose [34]. The aldehyde content of DACs from rice, wheat, and corn straw were 3.12, 3.34, and 3.87 mmol/g, respectively. After chlorite oxidizing the C2 and C3 aldehyde groups to carboxyl groups, the carboxyl content of DCCs from rice, wheat, and corn straw were 3.77, 3.89, and 4.03 mmol/g, respectively. The carboxyl content of DCCs is twice as large as the carboxyl content of CNFs prepared by TEMPO oxidation. The carboxyl is exposed on the outer surface, making it suitable for grafting of other functional groups or as an adsorption material, capable of adsorbing metal ion pollutants, cationic dyes and organic small molecule pollutants [40].

The carboxyl content measured here does not correspond to the aldehyde content. Based on the microfibrillar structure of cellulose, the maximum carboxyl content of the DCCs is calculated by theoretical analysis. Since the oxidation reaction with periodate and chlorite only occurs on the outer surface, the hydroxyl group exposed to the outside can be oxidized to a carboxyl group, with the

carboxyl groups concentrated on the outside of the microfibrils [34]. Due to the *gt* conformation of cellulose, only half of the hydroxyl groups at the C2 and C3 positions can be oxidized to carboxyl [41]. The cellulosic basic unit cellobiose is 1.03 nm in length [42]. Regardless of the lignin and hemicellulose residues in the purified cellulose, a microfibrillar structure composed of B elementary fibrils was set, and C roots were exposed. The average nanofiber crystal length obtained in the experiment was A nm. The relative molecular mass of a hydroglucose ring is 162, and NA is Avogadro's constant.

The mass of cellulose microfibrils of length A is given by

$$\frac{A}{1.03} \times 2 \times B \times \frac{162}{N_A} = \frac{314.555AB}{N_A};$$
(5)

with the number of carboxyl groups exposed given by

$$C \times \frac{A}{1.03} \times 2 \times \frac{1}{2} \times 2 = 1.9417AC;$$
 (6)

the theoretical carboxylic moles given by

$$n_{(-COOH)} = \frac{N_{(COOH)}}{N_A} \times 10^3 = \frac{1.9417AC}{N_A} \times 10^3 \text{ mmol};$$
(7)

and the theoretical carboxyl concentration (mmol/g) given by

$$c_{(-COOH)} = \frac{1.9417AC}{N_A} \times 10^3 \times \frac{N_A}{314.555AB} = \frac{6.1728C}{B} \text{ mmol/g.}$$
(8)

The carboxyl content of the DCCs is determined by the total number of microfibril structures and outer ring chains by Eq. (8). According to the cellulose molecular model of Nishiyama [43], the total number of molecular chains in the cross section is 36, and the total number of molecular chains in the outer circle is 20. The theoretical carboxyl content is 3.40 mmol/g. The average carboxyl content is between 3.8 and 4.0 mmol/ g in our experiments, and it is not affected by the type of raw material. The measured carboxyl content of the DCCs is higher than the theoretical value. The reason is that periodate is a strong oxidant. During the reaction, short-chain fibers or polysaccharide rings are degraded with the amorphous area of cellulose. The insolubility of these impurities results in them not being separated with the supernatant during centrifugation, and they remain in the solid solute after freeze-drying. The C2 and C3 hydroxyl groups on the glucose ring of these impurities are also treated by sequential periodate-chlorite oxidation, producing carboxyl groups, resulting in the final measured carboxyl content being the sum present in the DCCs and impurity content; therefore, the value of the actual measured carboxyl content is larger than the theoretical calculated value.

3.4 Transmission Electron Microscopy

Transmission electron microscopy was employed to examine morphological features and size distributions of different DCCs. As shown in Fig. 3, the DCCs prepared from rice, wheat, and corn straw appeared similar short-rod shape that were thicker in the middle and thinner at the ends. The periodate oxidation reaction proceeds in the first step mainly in the amorphous domain of cellulose and then goes to the crystalline phase [27,44]. Moreover, the rate of periodate oxidation at the crystal ends occurs about 10 times as fast as at the sides of the crystal [34]. Therefore, the morphological features of short rod with thicker in the middle and thinner at the ends were observed.

The length and diameter of DCCs from rice, wheat, and corn straw are shown in Tab. 1. The particle size frequency distribution is shown in Fig. 4. The average length of C-DCC is 135.0 nm, whereas it is 431.9 and 294.7 nm for W-DCC and R-DCC. The average length of C-DCC is the shortest among these three types of



Figure 3: TEM images of the (a) R-DCCs, (b) W-DCCs, and (c) C-DCCs



Figure 4: Particle size distribution curve of R-DCCs, W-DCCs, and C-DCCs

DCCs. This might be explained that corn straw has a complex composition, which is composed of corn leaf, stalk rind, and stalk pith. The fiber lengths of corn leaf $(0.86 \pm 0.03 \text{ mm})$ and stalk pith $(0.38 \pm 0.01 \text{ mm})$ are shorter than that of stalk rind $(1.11 \pm 0.01 \text{ mm})$ [45]. However, rice straw and wheat straw are hollow structures, and the main component is the stalk rind without pith. The average widths of W-DCC and C-DCC are similar, 7.9 and 8.4 nm, respectively, while the average width of R-DCC is 13.3 nm. Somerville et al. reported that the diameter of a single microfibril is about 3 nm in higher plants [46]. Thus, the DCCs prepared from rice, wheat and corn straw in this study are so-called microfibril aggregates [47]. The aspect ratio of wheat DCCs is 51.4. The aspect ratio of rice and corn DCCs were 22.2 and 17.1, respectively.

3.5 Thermogravimetric Analysis (TGA)

The thermal stability of purified cellulose, and DCCs from rice, wheat and corn straw was investigated by TGA, with the curves presented in Fig. 5. Based on the temperature-mass loss percentage change curve, each TGA curve can be divided into three regions. Region I is defined as the portion of mass loss that occurs at 50°C to 262°C. In region I, the mass loss is seen to be approximately 10%, due to the evaporation of water in the DCC samples. There is no thermal degradation of the DCCs in this area, and a plateau is observed. The termination temperature of region I is 262°C, which is defined as the degradation initiation temperature of DCCs. The thermal degradation stage of DCCs occurs from 262°C to 340°C, defined as region II. The mass loss in region II is approximately 70%. As the temperature further increases, the DCCs begin to undergo thermal degradation. With a decrease of the mass percentage of solid residues, the formation of CO_2 , H_2O , CO, and the formation of solid coke are detected. Region III is defined as the termination temperature region between 340°C and 600°C. In region III above 500°C, the final solid residue is approximately 20%.



Figure 5: TGA curves of purified cellulose and DCCs

The region I end temperature of purified cellulose was 326°C. The mass loss is approximately 5.5%, which indicates that the moisture content in the sample is 5.5%. In region I, purified cellulose has better thermal stability than DCCs in the low-temperature region. In region II, which is the main stage of thermal degradation of cellulose, which starts at 326°C and ends at 373°C, the mass loss is 81.5%. Region III starts at 373°C and ends at 600°C.

The thermal stability of purified cellulose is better than that of DCCs in the low temperature region, and the final mass residue is 13% and 20% for the purified cellulose and the DCCs, respectively. This phenomenon can be attributed to the fact that the surface of the DCC possesses a large number of carboxyl groups, which have better cross-linking properties, resulting in better thermal resistance at high temperatures [48].

3.6 DCCs Prepared from Agricultural Waste Used for Copper Removed

DCCs prepared by sequential periodate-chlorite oxidation have a large specific surface area and high carboxyl content. Since the positive-charged metal ions interact with the negative-charged carboxyl functional groups following the electrostatic attraction principle [49], DCCs can be used to adsorb metal cations in water. Therefore, the R-DCC, W-DCC, and C-DCC were investigated for the absorption of copper ions in aqueous medium. The adsorption capacities of copper ions were 131, 162, and 144 mg/g for R-DCC, W-DCC, and C-DCC, respectively.

The regeneration and reusability experiments were performed with W-DCC, which was subjected to 5 cycles of copper ions adsorption-desorption using 0.5 M HCl as eluent. The adsorption capacities after each cycle were 159, 155, 151, 149, and 146 mg/g. The adsorption capacity of W-DCC reduced from 162 to 146 mg/g (about 10%). After 5 cycles of regeneration, the adsorption capacity of W-DCC was still three times higher than that (46 mg/g) of the black wattle tannin-immobilized nanocellulose [50]. The results show that DCCs has good reusability when used as an adsorbent to remove copper ions from aqueous solutions.

4 Conclusions

Purified cellulose from agricultural waste straw was treated with sequential periodate-chlorite oxidation resulting in rod-like DCCs with an average length of 287.0 nm and width of 9.9 nm being prepared. The carboxyl content of the DCCs was around 3.9 mmol/g, and not affected by the type of straw. The carboxyl content of the DCCs reached more than 3 mmol/g, and nanocellulose was prepared without mechanical treatment. The sequential periodate-chlorite oxidation method can be applied to purified cellulose from different straw types. Due to the rich carboxyl groups on the surface of the DCCs, DCCs are suitable for removal of copper ions from aqueous medium. The adsorption capacities for copper ions were 131, 162, and 144 mg/g for the DCCs prepared from rice, wheat, and corn straws, respectively. The results show that DCCs prepared from rice, wheat, and corn straw by sequential periodate-chlorite oxidation have potential for use in the removal of copper ions from aqueous medium.

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