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# Influence of ultrasound treatment on accessibility and regioselective oxidation reactivity of cellulose

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**Abstract**

Cellulose fibers were treated with ultrasound in order to improve the accessibility and the reactivity of cellulose. The influence of ultrasound treatment on changes of morphology structure, accessibility and oxidation reactivity of cellulose with sodium periodate were discussed. The results revealed an increase in cellulose's accessibility in terms of water retention value (WRV) with increasing ultrasound treatment time, corresponding to 73.0%, 75.6%, 80.8%, 98.7% and 119.0% after treated for 0, 90, 180, 360 and 720 s, respectively. Furthermore, the regioselective oxidation reactivity of cellulose with sodium periodate was also successfully improved by the ultrasound treatment. However, no significant changes in crystallinity of cellulose were noted after ultrasound treatment. The oxidized products dialdehyde cellulose (DAC) was further characterized by means of FTIR, X-ray diffraction and SEM.


*Keywords:* Cellulose; Periodate oxidation; Ultrasound; Accessibility; Reactivity

## 1. Introduction

Cellulose, a homogeneous polymer of β-(1,4) glucose, is the most abundant biopolymer on Earth. Partial oxidation of cellulose constitutes one of the most versatile transformations since it provides access to various novel products and intermediates with valuable properties. There are numerous ways of oxidizing cellulose. However, only some methods are suitable for a regioselective oxidation of the chain units, while the glyco sidic linkages remain intact. The oxidation of cellulose by periodic acid and its salts leads to a product containing dialdehyde units called 2,3-dialdehyde cellulose (DAC) formed by oxidative cleavage at the C-2 and C-3 of the anhydro D-glucopyranose residues [1–3] (see Fig. 1). DAC is an important functional polymer for further derivatisation to specialized products such as 2,3-dicarboxy cellulose, and specialized applications [4,5].

However, the highly ordered structure and, particularly, the crystallinity of cellulose made it difficult to dissolve in ordinary solvent, and the cellulose reactions take place mostly under heterogeneous conditions [6]. Therefore it is generally recognized that some type of activating treatments is needed [7–9]. In the present work, water is used as a swollen reagent and an ultrasound is employed to treat cellulose fibers in order to improve cellulose's accessibility and reactivity. We aim to investigate the effect of ultrasound treatment on changes of structure, accessibility, and reactivity of cellulose with periodic salts.

## 2. Experimental

### 2.1. Materials

Cellulose fibers was prehydrolysis sulfate pulp from fast-growing eucalyptus with 97.6% of cellulose, 2.4%

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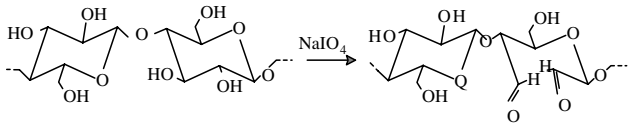



Fig. 1. Regioselective oxidation of cellulose by periodate.

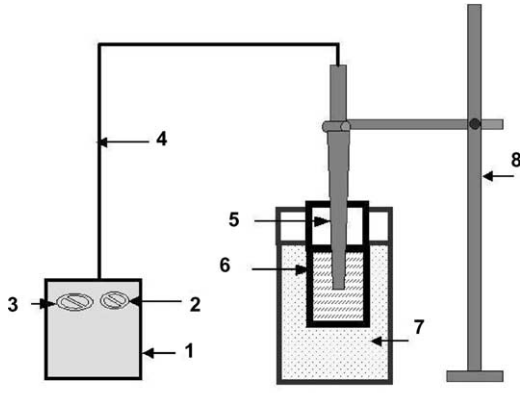
of hemicellulose (viscometric degree of polymerization, $DP_\eta = 754$). Sodium metaperiodate, and ethylene glycol were analytical-grade commercial products and were used without prior purification.

### 2.2. Apparatus

1. A ultrasound generator: JY88—I type bio-cell disrupter (manufactured by Ningbo Xin Zhi Sci and Equip Institute) with frequency of 23–25 kHz.
2. A centrifugal apparatus, type LG10—2.4 (manufactured by Beijing Medical Centrifugal Apparatus Factory).

### 2.3. Ultrasound treatment

Cellulose fiber was dispersed in water with a plastic tube (consistency was 1–2%), and then the suspension slurry was treated by an ultrasound (shown in Fig. 2). The ultrasound treatment was carried out in an ice bath to avoid overheating, and performed in a way of treating 30 s with 30 s cooling intervals. After the treatment, the suspension was washed with water, and the excess water was removed by centrifuging at 5350 rpm (centrifuging force = 3000 g) for 15 min. The centrifuged sample then was put in a brown reactor for the preparation of DAC.




1.Ultrasonic generator; 2. Time control unit;
3. Power control unit; 4. Cable connection;
5.Ultrasonic horn; 6. Process unit;
7. Ice bath; 8. Stand

Fig. 2. Schematic diagram of ultrasonic horn with variable power-output.

### 2.4. Water retention value (WRV) determination

The WRV of cellulose sample was determined according to the method described in reference [9] at 3000 g for 15 min.

### 2.5. Preparation of 2, 3-dialdehyde cellulose (DAC)

Periodate-oxidized cellulose was prepared by oxidizing 2 g of cellulose pulp (weights were corrected for moisture content) suspended in 0.11 mol/L–0.183 mol/L sodium periodate solutions with a liquor ratio of 38:1. The reaction mixture was kept at 60 °C for 1–5 h in the dark. After decomposition of the periodate excess with 7 ml ethylene glycol [1] and further reaction for 1 h, the oxidized products were filtered off, thoroughly washed with distilled water, ethanol and dried in vacuum at 45 °C, and a white, water insoluble, fibrous solid 2.3-DAC were obtained.

### 2.6. IR analysis

FTIR spectra were recorded on an Analect REX-65A FTIR spectrometer (KBr, after heating for 2.5 h at 105 °C, characteristic C=O at 1735 $cm^{-1}$).

### 2.7. Estimation of the dialdehyde groups

From the consumption of periodate [2] the amount of periodate consumed was determined by measuring the absorbency at 290 nm of the supernatant liquid. The periodiate consumed corresponds to the amount of dialdehyde groups generated. The oxidation extent was calculated accordingly in terms of Do, and its unit was mole CHO group per AGU (AGU = anhydroglucose unit).

### 2.8. X-ray diffraction

X-ray diffraction technique was employed in this work to investigate the crystalline structural changes of cellulose brought about by the ultrasound treatment. The X-ray diffraction data of the samples were recorded using a RIGAKU D/MAX-1200 diffractometer. The wavelength of the Cu/K radiation source was $1.5405 \times 10^{-10}$m and the spectra were obtained with an accelerating voltage of 40 kV. Samples were scanned on the automated diffractometer from 6° to 40° of $2\theta$, with data acquisition taken at intervals of 0.1° for 3 s. The crystalline structure of DAC was also characterized by X-ray diffraction. The crystallinity was calculated by the method of peak separation with a peak resolution program using Scherrer's equation [9].