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Extraction of cellulose from rice straw by microwave irradiation

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This article examines the process of converting large volumes of agricultural waste - rice straw - into cellulose which can be used for paper products manufacturing. The process of rice straw delignification is carried out using microwave irradiation at power levels of 100 and 180 W for 5-40 min with a sodium hydroxide solution. The delignification of the obtained product is also performed under microwave irradiation at power levels of 100 and 180 W for 5-40 min, using a mixture of acetic acid and hydrogen peroxide at a 1:1 ratio in the presence of ammonium molybdate (0-5 wt.% of cellulose mass). Concentrated sodium hypochlorite solution is used for bleaching of the obtained mass. The yield of the target product, cellulose, is 42.7-70.3 wt.%. The optimal product is cellulose obtained after delignification using a mixture of acetic acid and hydrogen peroxide in a 1:1 ratio under microwave irradiation with a power of 180 W for 15 min in the presence of ammonium molybdate (5% of the cellulose mass) and without using sodium hypochlorite. In this case, the content of alpha-cellulose in the final product is 74.45 wt.%, corresponding to Grade A2 (cellulose used for the production of white office paper). The obtained results have potential application in paper products manufacturing.

Keywords: rice straw, cellulose, microwave irradiation, paper products

INTRODUCTION

Cellulose, also known as plant fiber, is the main component of plant cell walls and, combined with other substances (incrustants), forms the structural framework of all plant organisms. In its purest form, cellulose is found, for example, in cotton fibers (up to 96-98%). Wood contains not only cellulose but also hemicellulose, lignin, resins, fats, proteins, and dyes. Dry wood contains about 40-60% alpha-cellulose, that is, cellulose insoluble in a 17.5-18% solution of alkali at room temperature [1]. To obtain high-quality cellulose, a bleaching process is crucial. Most factories use chlorine bleaching for this purpose, which allows obtaining highly purified cellulose. This method is used, for example, for producing kraft pulp and other grades [2]. Cellulose finds applications in various industries, such as pharmaceuticals (as an auxiliary substance in the production of medicinal products, suspensions, ointments, creams) [3], cosmetics (for creating creams, powders, suspensions, and other cosmetic products), food industry (in the production of mayonnaise, pastes, creams, canned meat, fish, dairy products, etc.), chemical industry (as raw material for further processing, including obtaining nanocrystalline cellulose, nanocomposites, ethers, copolymers), road coverings (to improve asphalt characteristics), and many other areas [4-7]. Rice is one of the key agricultural crops globally, providing sustenance for nearly half of the world's population. Its importance in production remains constant for both current and future food security concerns. In parallel with population growth, the demand for rice continues to increase, particularly in Asia and Africa [8]. However, the cultivation of rice poses various ecological challenges, such as the pollution caused by burning rice straw residues in fields. This issue is particularly complex and presents a significant challenge for technical experts in these regions. Nevertheless, numerous alternatives to burning straw are being explored, and research is being conducted to assess ways to reduce the environmental impact of rice production.

In recent times, various methods for converting rice waste into valuable products have been proposed. Our team has previously conducted work

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on transforming rice waste into a promising fertilizer - biochar, and a widely applicable adsorbent - activated carbon [9-12].

In this study, we propose the processing of rice straw into cellulose by carrying out processes of desiliconation with sodium hydroxide solution, and delignification with a mixture of acetic acid and hydrogen peroxide under microwave irradiation. Microwave activation of many organic processes is a rapidly developing field, allowing process durations to be reduced by orders of magnitude [13].

MATERIALS AND METHODS OF RESEARCH

To obtain cellulose from rice straw, the latter was initially crushed using a DKU-05 grinder (Russia). Then the crushed mass was washed with water and dried at a temperature of 25°C. Subsequently, 10 g of the crushed, washed, and dried rice straw were placed into a glass container, and 130 ml of sodium hydroxide solution with a concentration of 0.1 mol/L was added. The delignification process was conducted by irradiating the mixture with microwave beams at power levels of 100 and 180 W for 5-40 min. After irradiation, the decalcified cellulose mass was cooled to a temperature of 25°C, washed with distilled water until neutral pH, and then dried at 25°C. The resulting product was subjected to a delignification process, wherein 130 ml of a mixture of icy acetic acid and 37% hydrogen peroxide in a 1:1 ratio, along with ammonium molybdate (0-5% of the dry decalcified cellulose mass), was irradiated with microwave beams at power levels of 100 and 180 W for 5-40 min. Subsequently, the cellulose mass was washed until neutral pH. A saturated solution of sodium hypochlorite was added to the purified dry mass for bleaching (in some cases no bleaching was required). The yield of the final product ranged from 42.7% to 70.3%. The content of alpha-cellulose was determined by treating the obtained cellulose with a 17.5% sodium hydroxide solution (purged of carbonates) for 30 min followed by washing with distilled water and treatment with a 10% acetic acid solution for 30 min. After treatment, the cellulose was washed with distilled water and dried at a temperature of 105-135°C until a constant mass was achieved. The obtained mass was then weighed using analytical scales to determine the yield of alpha-cellulose [14]. IR spectra were taken on an IR-Prestige 21 instrument of Shimadzu (Japan, 2008) in the wavelength range 400-4000 cm^{-1} without special preparation of the sample on the DuraSamplIR II attenuated total reflection (ATR) module with a single reflection (prism material is diamond on ZnSe substrate) of Smiths (USA). To study the surface morphology of cellulose samples, SEM analysis was performed, and microphotographs were taken on a JSM-6510 LV device manufactured by Jeol (Japan). Measurements were carried out in high vacuum mode using a secondary electron detector at an accelerating voltage of 25 kV. The crystal structure of MCC was studied by X-ray diffraction on an X΄PertPRO diffractometer (Malvern Panalytical Empyrean, Netherlands) using monochromatized copper (CuKα) radiation with a scan step of 0.02°, K-Alpha1 [Å] 0.1542. The measurement angle was 10-40°, the X-ray tube voltage was 40 kV, the current intensity was 30 mA, the measurement time at each step was 0.5 s and an aluminum rectangular multi-purpose sample holder (PW1172/01) was used for the measurement in reflection mode.

RESULTS AND DISCUSSION

Various methods for producing cellulose are known, involving the use of cereal straw, cane crops or oilseeds, for example wheat straw, sunflower husks. In these methods, the straw is subjected to autohydrolysis at 180-220°C, pressures of 10-20 atm, and durations of 5-15 min, followed by pressure release. The autohydrolyzed mass is then twice extracted with dilute 0.4-1% NaOH solution or an organic lignin solvent (such as acetone, dioxane, ethyl alcohol, etc.). Subsequently, the mass is washed with distilled water and treated with a standard hydrogen peroxide bleach solution, followed by washing and drying at a temperature of 25°C. As the aqueous extract contains primarily autohydrolyzed sugars, it can be of significant interest for yeast production or as animal feed additive [15-17].

However, these methods have drawbacks, including technological complexity, use of specific autoclave equipment, elevated pressure, high temperature, and prolonged duration.

This study provides data on the extraction of cellulose from rice straw using microwave irradiation. Delignification is carried out using a 4 wt.% potassium hydroxide solution for 10-40 min at an irradiation power of 480 W. Subsequently, the material is treated with a 2.5 wt.% hydrogen peroxide solution and left for one night, followed by irradiation for 10 min at 480 W. Afterward, the material is washed with water until neutral pH and then dried under vacuum. Acidic treatment with acetic acid is conducted for 10-40 min at an irradiation power of 480 W. The material is then centrifuged, washed with water, and dried at a temperature of 25°C. Depending on the conditions, the product yield ranges from 48.6% to 67.3% [18]. Drawbacks of this approach include the use of the more expensive potassium hydroxide instead of sodium hydroxide, higher power levels of microwave irradiation, extended process duration, and relatively low product yield.

The present study addresses these drawbacks by irradiating the material with microwave beams at power levels of 100-180 W for 5-40 min, using a 1:1 ratio of icy acetic acid and 37% hydrogen peroxide (10% and 50% aqueous solution, respectively), applying ammonium molybdate as a catalyst (0.1%, 1%, and 5%), and sodium hypochlorite for bleaching (in some cases, the use of a mixture of hydrogen peroxide and acetic acid did not give the required whiteness, therefore a 10% sodium hypochlorite solution was used).

To determine the optimal conditions for obtaining cellulose from rice straw, a series of experiments were conducted, as detailed in the table. The obtained products were analyzed for alpha-cellulose content according to the method [14]. Based on the results of the experimental investigations, the products obtained under the conditions specified in items 12, 13, and 15 of the table correspond to Grade A2 cellulose, which is used for the production of white office and laboratory filter paper. The products obtained according to items 14 and 16 correspond to Grade B2 cellulose, used for manufacturing paper napkins, towels, school notebooks, toilet and laboratory filter paper. The products obtained according to items 1-11 and 17-23 correspond to unbleached cellulose, used for producing wrapping (kraft) paper and cardboard products [19].

A photograph of the obtained products, as specified in the table, is provided in Figure 1.

Table Determination of optimal conditions for cellulose extraction from rice straw under microwave irradiation

№	Microwave radiation power, (W)	Duration, (min)	Catalyst, (%)	Sodium hypochlorite, (ml)	Ratio of acetic acid to hydrogen peroxide (H_2O_2)	Yield of the target product, (%)
1	100	5	5	100	1:1	70.30
2	100	10	5	100	1:1	61.01
3	100	15	5	100	1:1	61.32
4	100	20	5	100	1:1	57.26
5	100	25	5	100	1:1	50.98
6	100	30	5	100	1:1	54.68
7	100	30	5	no chlorine	1:1	59.66
8	100	35	5	100	1:1	53.53
9	100	40	5	100	1:1	57.51
10	180	5	5	100	1:1	61.77
11	180	10	5	100	1:1	57.22
12	180	15	5	-	1:1	46.01
13	180	20	5	-	1:1	46.05
14	180	15	1	-	1:1	47.06
15	180	15	0,1	-	1:1	47.95
16	180	15	-	-	1:1	42.77
17	180	15	-	100	10% aqueous solution of mixture	62.62
18	180	15	-	-	50% aqueous solution of mixture	62.89
19	180	15	-	100	50% aqueous solution of mixture	59.59
20	180	20	-	-	50% aqueous solution of mixture	62.79
21	180	20	-	100	50% aqueous solution of mixture	51.59
22	180	25	-	-	50% aqueous solution of mixture	68.96
23	180	25	-	100	50% aqueous solution of mixture	51.48

Figure 1. Photograph of the obtained products according to the table

The cellulose obtained according to item 12 of the table exhibited notable whiteness. Due to this, an analysis was conducted on this product to determine its alpha-cellulose content in accordance with the methodology [14]. The alpha-cellulose content in this product was measured to be 74.75%, which corresponds to Grade A2 cellulose.

The IR spectrum shows absorption bands at 663 cm^{-1} (C-OH bonds), 898 cm^{-1} and 1157 cm^{-1} (glycosidic C-O-C), an intense band at 1029 cm^{-1} (pyranose C-O), 1226 cm^{-1} and 1319 cm^{-1} C-H bond vibrations, 1431 cm^{-1} vibrations of CH_2, 1647 - OH due to water molecules sorbed from air, 2846 absorption band of CH-, broad absorption band of associated -OH group in the region of 3000-3500 cm^{-1} (Figure 2).

The surface morphology of the cellulose obtained from rice straw is shown in Figure 3. The cellulose fibers are 3-5 μm wide and the surface is clean and relatively smooth.

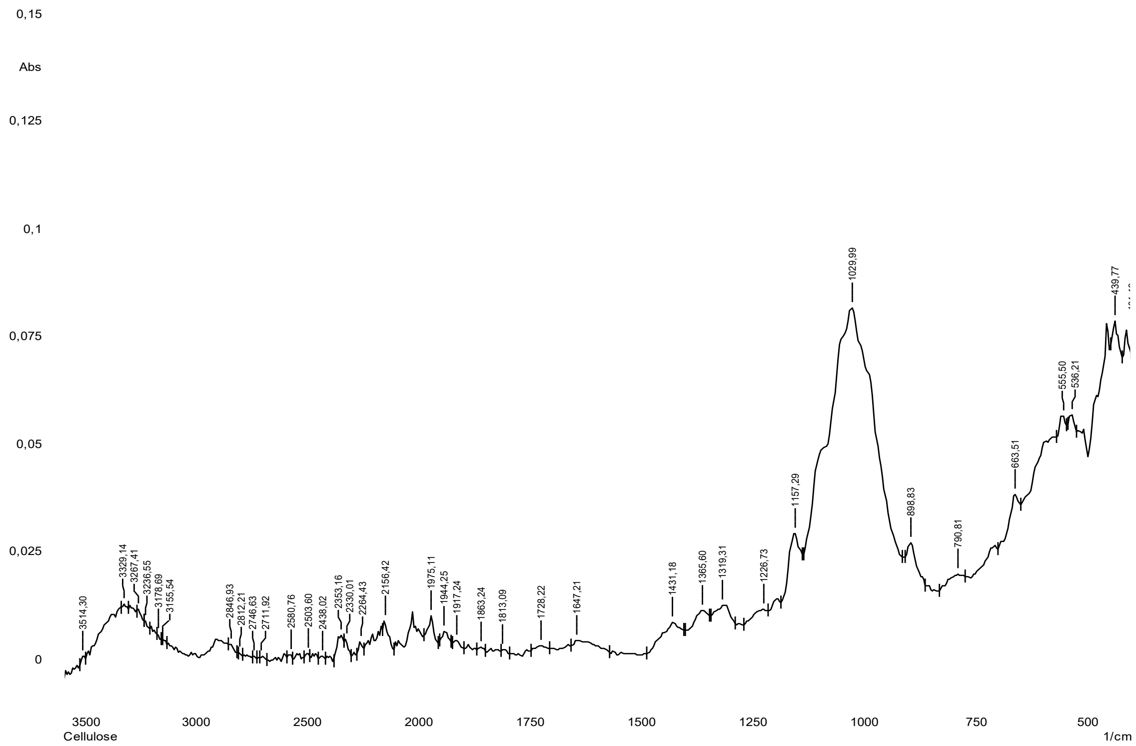

Figure 2. IR spectrum of cellulose obtained from rice straw under optimal conditions

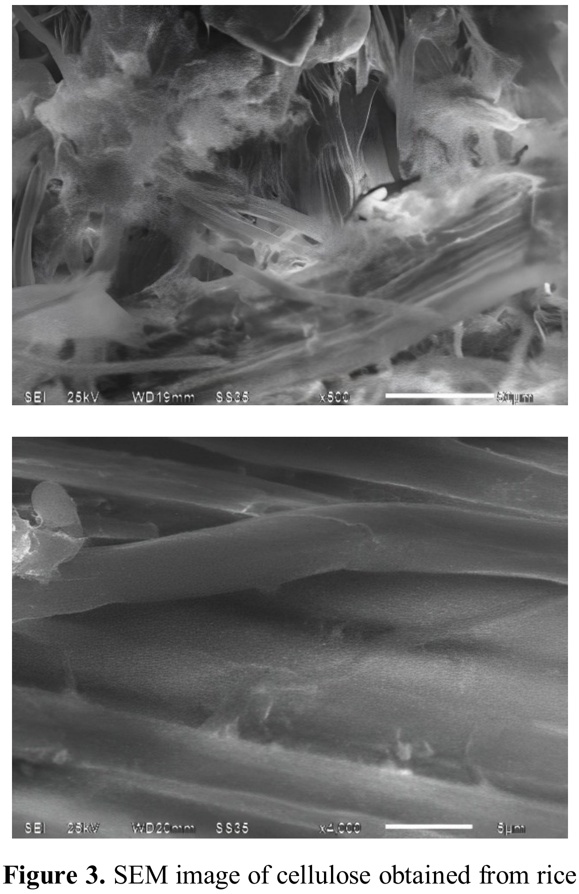

Figure 3. SEM image of cellulose obtained from rice straw under optimal conditions

On the X-ray diffraction pattern of the obtained MCC in Figure 2 three diffraction peaks were registered. They are equal to 2θ=15.5^0, 21.7^0, 34.7^0 and the crystal structure of the molecule is double-stranded monoclinic, cellulose I β showed diffraction peaks [17, 20]. The crystal structure of the MCC obtained in the refs. [21, 22] is consistent with the results of the present study. This indicates that the crystal structure of the material obtained in this investigation is typical for MCC (Figure 4).

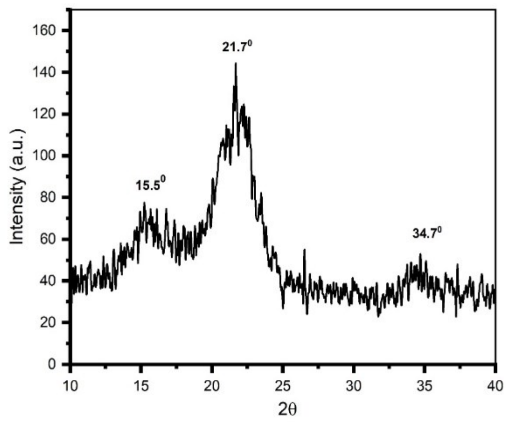

Figure 4. X-ray diffraction pattern of cellulose obtained from rice straw under optimal conditions

CONCLUSION

The proposed method for obtaining cellulose from rice straw offers several advantages compared to known methods:

- It utilizes agricultural waste in the form of rice straw;
- The use of microwave irradiation enhances energy efficiency;
- The process duration is significantly reduced;
- The sodium hydroxide concentration required for delignification is lowered;
- High pressure is eliminated from the delignification process;
- The catalyst quantity in the delignification process is reduced or eliminated;
- Reduced amounts of hydrogen peroxide and acetic acid are used in the delignification process.

The results of the experimental research not only facilitate the rational utilization of natural resources but also hold environmental significance. Furthermore, the approach aligns with the principles of green chemistry.

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