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CELLULOSE FIBERS EXTRACTED FROM AGRICULTURAL BIOMASS

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Scientific paper

Abstract: *The agricultural biomass is an important and inexpensive source of cellulose and cellulose fibers. Therefore, many efforts are made to replace at least a portion of synthetic fibers with cellulose fibers obtained from plant waste materials. This paper presents the study of cellulose fibers extracted from plant agricultural biomass including: wheat, rape, rice, sunflower and flax straws. In this paper, the selected materials were treated by the very common method who include consecutive physicochemical techniques to remove non-cellulosic components such as pectic substances, lignin and hemicellulose, as well as to obtain cellulosic material with suitable structure and properties necessary for preparing cellulose micro- and nanofibers. It has been shown that the use of chemical treatment using sodium chlorite ($NaClO_2$) as delignification agent, allowed the safe removal of non-cellulosic components without degradation of the cellulose fibers. Therefore, an efficient utilization of such agricultural wastes is of great importance not only for minimizing the environmental impact, but also for obtaining a higher profit.*

Keywords: agricultural biomass, cellulose fibers, purification, delignification.

CELULOZNA VLAKNA EKSTRAHOVANE IZ POLJOPRIVREDNE BIOMASE

Apstrakt: *Poljoprivredna biomasa je važna i jeftin izvor celuloze i celuloznih vlakana. Zbog toga, mnogi napori su napravljene da zameni bar deo sintetičkih vlakana sa celuloznih vlakana dobijenih od biljnih otpadaka. Ovaj rad pretstavlja proučavanja celuloznih vlakana ekstrahovane iz biljne poljoprivredne biomase, uključujući: pšenične, repine, orizove, suncokretove i lenene slame. U ovom radu, odabrani materijali su tretirani od strane veoma česta metoda koja obuhvata uzastopne fizikohemijske tehnike za uklanjanjene ne-celulozne komponente kao što su pektinske materije, lignina i hemiceluloze, kao i da dobiju celuloznih materijala sa odgovarajućim struktura i svojstva potrebne za pripremu celulozne mikro- i nanovlakana. Pokazano je da korišćenje hemijski tretman korišćenjem natrium hlorit ($NaClO_2$) kao sredstvo za udaljavanje lignina (delignifikacija), omogućio je bezbedno uklanjanje ne-celulozne komponente bez degradacije celuloznih vlakana. Dakle, efikasna upotreba takvih poljoprivrednih otpada je od velikog značaja ne samo za minimiziranje uticaja na životnu sredinu, ali i za dobijanje veći profit.*

Ključne reči: *poljoprivredna biomasa, celulozna vlakna, pročišćavanje, udaljavanje lignina.*

1. INTRODUCTION

Lignocellulosic fibers have become the focus of intense interest in recent years. They have attracted the attention of scientists and technologies worldwide because of their tremendous advantages and now it is possible to isolate cellulose nanofibrils and nanowhiskers from various lignocellulosic wastes.

Agricultural and industrial wastes are generated in huge quantities in Macedonia and other countries. Generally they are not reused or recycled. Interest arises in waste sources from the biomass left behind. This waste tends to be an environmental problem as it has strong fibers which breakdown very slowly under natural conditions. Lignocellulosic materials are well known for their abundance, availability, economic and environmental advantages. These renewable feed stocks, including wood and agricultural biomass such are the major resources for cellulose fibers. In the last decade many studies have been done on extracting cellulose. The aim of this study was to determine the chemical composition of biomass plant materials from different agricultural waste sources as (wheat, rape, rice, sunflower and flax straws) in terms of their suitability to extract cellulose fibers. The cellulose fibers obtained from waste materials can be used in the preparation of micro- and nano- cellulose fibers.

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Cellulose is one of the most widespread biopolymer found globally, existing in a variety of living species such as plant, animals, bacteria and some amoebas [1]. Cellulose is one of the most abundant polymers on the earth and is well known for its industrial use such as in pulp and paper, textile, bio ethanol and so on. Cellulose is the primary component of the cell walls of higher plants. Natural fibers mainly consist of cellulose, lignin, and hemicellulose but also include low quantities of pectin, pigments and extracts. Cellulose chains in the plant cell wall are aggregated into a repeated crystalline structure to form the micro fibrils and are interconnected through the loosely arranged cellulose, hemicellulosic and lignin network. The microfibrils further aggregate on the macroscale to form fibers. The natural fibers themselves act as composite materials, assembling in a mainly lignin matrix [2]. This hierarchical structure has to be destructed to generate cellulose microfibrils from this network. Many method have been suggested in the literature to-date including, chemical, mechanical, physico-chemical treatments.

The chemical composition of lignocellulosics is inherent according to the particular needs of the plants. Lignocellulose is the primary building block of plant cell walls. Plant biomass is mainly composed of cellulose, hemicellulose, and lignin, along with smaller amounts of pectin, protein, extractives (soluble nonstructural materials such as non-structural sugars, nitrogenous material, chlorophyll, and waxes), and ash. The composition of these constituents can vary from one plant species to another. In addition, the ratios between various constituents within a single plant vary with age, stage of growth, and other conditions [3].

Lignocellulosics are used for various applications, depending on their composition and physical properties. Wheat and rice straw, and even corn stalks to a limited extent, have traditionally been used for pulp and paper making [4]. Recently, natural cellulose fibers suitable for textile and other industrial applications have been produced from corn husks and corn stalks [5, 6]. Rice and wheat straw have also been used to produce regenerated cellulose fibers as an alternative to wood for cellulose-based materials [7].

Natural cellulose fibers are extracted from lignocellulosic byproducts using bacteria and fungi, mechanical and chemical methods. Retting, the traditional process to extract fibers, uses bacteria and fungi in the environment to remove lignin, pectin and other substances [8].

Consumer awareness is still increasing, and more and more people want to buy environmentally friendly products. The increased use of agricultural fibers is one of the ways to give consumers a wider choice of environmentally friendly products. Even assuming that only about 10% of all products which are suitable for the production of fibers, and the yield of the process of about 20%, possibly up to 50 million tons per year of technical cellulose fibers can be obtained from only four cereals (rice, wheat, soybeans, and corn) [9]. The first reports on the isolation of cellulose microfibrils date back to 1983 with the starting material being wood cellulose (softwood) [10].

2. EXPERIMENTAL PART

2.1. Materials

Different agricultural biomass material: wheat straw, rape straw, rice straw, sunflower straw and flax straw.

2.2. Treatment methods

Purification of the non-cellulosic components of the biomass material. The sample of about 1 kg of biomass was placed in a digester with a capacity of 27 dm^3 and treated with steam at 0.3-0.4 MPa for 15 minutes. The steamed pulp was soaked in hot water overnight and subjected to refining in a laboratory mill at a gap width of 0.1 to 0.5 mm.

Chemical treatment of the biomass material.

Sodium hydroxide/hydrogen peroxide digestion method (SH/HP) was performed in a digester with a capacity of 27 dm^3. The pulp sample after pre-steaming was placed in a container and a cooking liquor was added at about 65 °C (6% NaOH, 6% H_2O_2, 0.5% EDTA, 1% $MgSO_4$ and 5% liquid glass, per sample of dry weight. The pulp was stirred for about 15 minutes. The liquor ratio to material was 4:1. After that, the pulp was placed in the digester and cooked at 110 °C for 80 minutes.

Sodium hydroxide digestion method (SH) was performed in a digester with a capacity of 27 dm^3. The pulp sample after pre-steaming was placed in a container and a cooking liquor was added at about 65 °C (8% NaOH, per sample of dry weight). The pulp was stirred for about 15 minutes. The liquor ratio to material was 4:1. After that, the pulp was placed in the digester and cooked at 100 °C for 80 minutes.

Sodium chlorite delignification of the biomass material (SHl-D)**.** The pulp sample after pre-steaming and digesting delignification was centrifuged and was added to distilled water at about 65 °C, and was added 16 g/dm^3 $NaClO_2$ and 3.5 g/dm^3 H_2SO_4, and the pulp was placed in a laboratory thermostat at a temperature of 75 °C for 150 min. Centrifuged and weighed pulp was added to distilled water at about 65 °C, and was added 2% NaOH, per sample of dry weight. After that, the pulp was placed in a laboratory thermostat at a temperature of 75 °C for 150 min.

2.3. Chemical analyses

Analysis of chemical composition of biomass samples before and after chemical treatment were conducted according to the following standards:

- the contents of lignin, cellulose, holocellulose, substances soluble in organic solvents and mineral substances (PN-92/P-50092:1992)
- the content of alpha-cellulose (PN-62/P-50099:1962)

3. RESULTS AND DISCUSSION

3.1. Chemical composition of different types of plant biomass

Cellulose, hemicellulose and lignin are the three main constituents of any lignocellulosic source. Cellulose is the main structural component that provides strength and stability to the plant cell walls and the fiber. The amount of cellulose in a fiber influences the properties, economics of fiber production and the utility of the fiber for various applications. For example, fibers having higher cellulose content would be preferable for textile, paper and other fibrous applications. Hemicellulose in plants is slightly crosslinked and is composed of multiple polysaccharide polymers with a degree of polymerization and orientation less than that of cellulose [11]. Mechanically, hemicellulose contributes little to the stiffness and strength of fibers or individual cells [12]. Lignin is a highly crosslinked molecular complex with amorphous structure and acts as glue between individual cells and between the fibrils forming the cell wall [13]. The lignin content of the fibers influences the structure, properties, morphology, flexibility and rate of hydrolysis [14]. Fibers with higher lignin content appear finer and will be more flexible [14]. Mineral substances present in lignocellulosics, especially straw, contains silica that has many undesirable effects [15]. Such raw material is less susceptible to loosening and swelling of the fibre structure [15].

Chemical composition of different types of plant biomass (wheat straw, rape straw, rice straw, sunflower straw and flax straw) is shown in *Table 1*.

Table 1.- *Chemical composition of different types of plant biomass*

Plant biomass	Lignin, %	Holocellulose,%	Alpha-cellulose, %	Soluble substances in ethanol, %	Mineral substances, %
Wheat straw	21.65	73.75	39.17	4.57	5.53
Rape straw	19.43	72.28	45.39	3.32	4.27
Rice straw	15.65	59.13	38.42	8.56	13.25
Sunflower straw	18.24	69.33	40.16	7.51	6.89
Flax straw-fiber variety	17.81	75.89	58.74	3.72	2.84

Among all studied materials, flax straw, and rape straw were characterized by a favorable composition for the isolation of cellulose fibres intended for conversion into cellulose nanofibres.

The alpha-cellulose content was 58.74% for retted flax straw-fibre variety and 45.39% for rape straw. The lignin content in these two materials was 17.81 and 19.43%, respectively (*Table 1*). The organic substances content in the retted flax straw-fibre variety was 3.72% and in rape straw it was 3.32%, which was lower than in the other raw materials (*Table 1*). High cellulose content and low content of lignin as well as organic and inorganic substances indicate the suitability of biomass for the production of cellulose fibres. The presence of significant amount of organic substances soluble in ethanol (>7%) inhibits the delignification process.

3.2. Purification and isolation of cellulose fibres from biomass samples

The amount of cellulose and non-cellulosic constituents in a fiber determine the structure and properties and influence its crystallinity and moisture regain [16]. Generally, fibers with higher cellulose content, higher degree of polymerization of cellulose and lower microfibrillar angle give better mechanical properties [14]. Cellulosic fibers change their dimensions and properties with varying moisture content [13]. Moisture content in fibers influences the degree of crystallinity, crystallite orientation, tensile strength, swelling behavior and porosity of vegetable fibers [14].

Purification of biomass samples from non-cellulosic components was performed using two methods: with sodium hydroxide/hydrogen peroxide (SH/HP) and sodium hydroxide (SH). Initially, biomass was subjected to steaming and grinding. Mechanical treatment and the steaming process modifies the structure of fibres. Cellulose fibres of a uniform structure can be obtained through the grinding process. Using chemical treatment of biomass samples we attempted to compare the purifying and delignification effects.

In the case of the (SH/HP) method a decrease in lignin content was observed: from 21.65% to 17.08% for wheat straw, from 19.43% to 12.93% for rape straw, from 15.65% to 12.78% for rice straw, from 18.24% to 14.89% for sunflower straw and from 17.81% to 12.79% for flax straw- fiber variety (*Table 2*).

Table 2.- *Lignin content after chemical treatment by sodium hydroxide /hydrogen peroxide (SH/HP) and sodium hydroxide (SH) methods*

Plant biomass	Lignin contents, %		
	Starting value	SH/HP method	SH method
Wheat straw	21.65	17.08	18.45
Rape straw	19.43	12.93	13.21
Rice straw	15.65	12.78	13.25
Sunflower straw	18.24	14.89	15.22
Flax straw-fiber variety	17.81	12.79	14.27

The pulps obtained from flax and rape straws were characterized by high alpha-cellulose content (76.34% and 74.51%, respectively), and other pulps obtained from wheat straw, rice straw and sunflower straw had a low alpha-cellulose content (below 50%) (*Table 3*). This shows that the purification degree depends mainly on the biomass type. The low level of alpha-cellulose content indicates that the cellulose structure might be damaged.

Table 3.- *Alpha-cellulose content after chemical treatment by sodium hydroxide /hydrogen peroxide (SH/HP) and sodium hydroxide (SH) methods*

Plant biomass	Alpha-cellulose contents, %		
	Starting value	SH/HP method	SH method
Wheat straw	39.17	49.25	44.13
Rape straw	45.39	74.51	69.37
Rice straw	38.42	43.72	41.28
Sunflower straw	40.16	45.23	43.39
Flax straw-fiber variety	58.74	76.34	69.48

The (SH/HP) method treatment was more effective compared to the (SH) method because in the (SH/HP) method a higher degree of lignin removal, and an increase in alpha-cellulose content was obtained.

Incomplete removal of lignin from the biomass implies the necessity for further purification stages. The next delignification steps were carried out with the use of two-step sodium chlorite treatment (SHl-D). As a result of these treatments, pulps obtained from flax and rape straws had a low amount of residual lignin, (3.45% and 3.71%, respectively), while increasing alpha-cellulose content (79.93% and 78.21%, respectively) (*Table 4*). This can significantly facilitate further processing of pulps into micro and nanofibres.

Table 4.- *Lignin content and alpha-cellulose content after sodium chlorite delignification (SHl-D)*

Pulp sample	Lignin contents, %		Alpha-cellulose contents, %	
	SH/HP method	SHl-D	SH/HP method	SHl-D
Flax straw-fiber variety	12.79	3.45	76.34	79.93
Rape straw	12.93	3.71	74.51	78.21

4. CONCLUSIONS

The major limitations of using agricultural byproducts are the lack of an established collection, storage, and handling systems that would prevent the degradation of the lignocellulosics when stored for a considerable period.

The potential availability and economics of using agro-based fibers far outweigh their limitations. An increasing population and restrictions on using natural resources to grow fiber crops make agro-based fibers the most promising alternative to natural fibers.

The analysis of the chemical composition of some agricultural biomass (wheat, rape, rice, sunflower and flax straws) have shown that the most suitable raw materials for obtaining cellulose fibres are: flax straw-fibre variety and rape straw.

The application of the sodium hydroxide/hydrogen peroxide method compared with the sodium hydroxide method facilitated the purification of plant materials from non-cellulosic components. The use of two-step sodium chlorite treatment of biomass plant as delignification agent allowed to safely remove lignin and other non-cellulosic components, without degradation of obtained the cellulose fibres.

The future seems to be bright for biofibers from agricultural biomass.

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