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CHEMICAL TECHNOLOGY: SCIENCE, ECONOMY AND PRODUCTION

ЗБІРНИК НАУКОВИХ ПРАЦЬ

VI Міжнародної науково-практичної конференції

ХІМІЧНА ТЕХНОЛОГІЯ: НАУКА, ЕКОНОМІКА ТА ВИРОБНИЦТВО

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Збірник наукових праць VI Міжнародної науково-практичної конференції «Хімічна технологія: наука, економіка та виробництво», м. Шостка, 23 - 25 листопада 2022 року. – Суми : Сумський державний університет, 2022. – 267 с.
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Збірник містить наукові праці учасників VI Міжнародної науково-практичної конференції «Хімічна технологія: наука, економіка та виробництво», що складаються з узагальнених матеріалів науково-дослідних робіт науковців різних галузей виробництв та наукових закладів України.

У збірнику висвітлюються актуальні питання спеціальної хімічної технології і виробництва боєприпасів, утилізації відходів виробництв різних галузей, енергозбереження, моделювання технологічних процесів, соціально-економічні аспекти виробництва та природокористування в умовах війни.

Збірник корисний робітникам хімічної промисловості, науковим співробітникам, аспірантам і студентам спеціальностей хіміко-технологічного та соціально-економічного профілів, фахівцям інформаційних технологій виробництва.

Наукові праці учасників конференції подаються в авторській редакції.

STUDY OF THE PROCESS OF OBTAINING CELLULOSE FROM THE SEA GRASS ZOSTERA MARINA BY THE METHOD OF CATALYTIC DELIGNIFICATION

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Introduction. Cellulose is the most common biopolymer used worldwide on an industrial scale with applications in sectors such as paper, fabric, cosmetics and pharmaceuticals, explosives, etc. [1]. About 10^{12} tons of pulp are produced annually from various natural sources, mainly from plants and trees. In fact, for decades the most important source of raw pulp production has been wood, accounting for 2% (approximately 3.2 million tons/year) of annual production. Environmental concerns related to the increased use of wood sources have led researchers to explore new options, including non-wood and residual material sources, such as agricultural and forest residues or clippings from woody species or grasses.

The insufficient amount of raw materials is the main problem of all enterprises of the pulp industry in Ukraine. Countries that do not have a good raw material base from wood find a more promising direction of obtaining cellulose from non-wood plant raw materials. China, which produces paper from rice straw, Indonesia, Australia, South Korea, India and Japan are the world leaders in the use of agricultural waste and annual plants in the pulp industry [2].

In Ukraine, the search for new raw materials for the production of cellulosic materials continues. Thus, the technology of producing cellulose from straw was developed in international cooperation [3]. At the National Technical University "KPI" they developed a technology for making packaging paper from sunflower stalks [4]. An innovative project of 100% waste-free environmentally friendly production of pulp using industrial hemp as raw material was developed by the Institute of Bast Cultures in Glukhiv under the leadership of the Ukrainian Academy of Agrarian Sciences [5].

Ukraine also started production of eco-friendly paper from fallen leaves. The technology was proposed by a young scientist Valentyn Frechka [6].

But paper products are not the only way of using cellulosic materials. In particular, cellulose serves as a raw material for the production of most types of gunpowder. By nitrating cellulose, its nitrates are obtained - explosive substances, from which powder elements are formed by plasticizing with solvents. In Ukraine, there is no pulp raw material base and pulp and paper mills for its processing, which are necessary for the powder industry.

Marine plants as an alternative raw material for obtaining cellulose.

Currently, almost all possible sources of cellulose are of terrestrial plant origin. But ocean resources can offer significant potential for cellulosic materials.

Cellulose is contained in every plant, but industrial extraction of this polysaccharide is not possible from every plant. When choosing raw materials, it is necessary to rely on the fiber content, structural features of its fiber components, the possibility of using industrial processing methods, the quality of the product obtained as a result of this processing, the prevalence of plant raw materials, the cost of its collection and storage.

The use of algae as a raw material for obtaining cellulose has been considered in many countries. Thus, in China, a method of obtaining cellulose from red algae was developed, and the production of a new cellulose nanomaterial from marine biomass of red algae Gelidiumelegans was proposed [2].

One of the possible sources of cellulose is coastal deposits of the sea grass Zostera marina, and this paper presents a study of the possibility of obtaining it.

Zostera marina is a perennial marine herbaceous plant. It grows in shallow water along the coast of the Black and Azov seas.

Zostera marina sea grasses are flowering plants (angiosperms). They can be found in most oceans and it are the only angiosperms that have adapted to the marine nature of the environment [7]. Zostera marina is not a direct food source, at least during cultivation, due to its high cellulose content, low nitrogen content, and presence of phenolic acids. Therefore, grasses usually degrade at the end of their life cycle. In some coastal regions, especially along the coasts of the Black and Azov seas, deposits of sea grass washed ashore on beaches after storms are pollution that requires regular removal and disposal. Therefore, alternative use of this resource is of interest.

According to the results of the literature search, it is relevant to study the possibility of obtaining cellulose from the grass Zostera marina. Unlike algae, sea grass is closer in origin to land plants. According to various literary sources, the cellulose content in sea grass is 25-40% [8]. But just like algae, sea grass contains a much lower percentage of lignin than land plants. This can be used to obtain cellulose products for special purposes, as well as cellulose for further chemical processing. By processing grass mass, it is possible to produce fillers into synthetic polymers, which ensure the biological decomposition of polymer compositions and necessary in the production of materials with an adjustable service life, as well as to obtain cellulose semi-finished products used as raw materials for the chemical industry, in particular, the production of cellulose nitrates.

In previous studies at the institute, paper samples were obtained by soft delignification of raw materials with hydrogen peroxide solutions [9-10].

The results of the research made it possible to consider the possibility of obtaining cellulose samples from the sea grass Zostera marina in laboratory conditions, with the aim of their further use in the chemical industry, in particular for the production of cellulose nitrates.

An indicator of the quality of cellulose for nitration is a high percentage of α-cellulose in the obtained product. Previously, a series of experiments was conducted to vary the technological parameters of the process at the level of a small volume [11]. Based on the conducted experiments, an indicative research plan was developed.

Standard technologies of oxidative delignification of wood were taken as the basis of the process. The production of cellulose was carried out by the method of soft delignification with a solution of hydrogen peroxide in the presence of catalysts.

Raw material preparation includes pre-washing the grass with fresh water, sifting to remove sand, drying to a constant mass at room temperature, mechanical grinding.

Research methodology. The process is based on standard technologies of oxidative delignification of wood [12]. The production of cellulose was carried out by the method of soft delignification with a solution of hydrogen peroxide in the presence of catalysts.

Dry deposits of Zostera Marina seagrass, collected on the coast of the Karkinit Bay, were used as the research object. They are an elastic mixture of ribbon-like leaves of brown color.

Preparation of raw materials includes preliminary washing of grass with fresh water, sifting from sand, drying to a constant mass at room temperature, mechanical grinding.

In [8], the structure of plant fiber obtained from Zostera marina grass was studied. This seagrass species has been found to have small diameter (about 5 μm) fibers consisting of ∼57% cellulose, ∼38% non-cellulosic polysaccharides (mainly xylan) and ∼5% residual material, the so-called Clason lignin.

In order to clarify the cellulose content in the raw material, an analysis was carried out by the Kürschner and Hanek method. The average cellulose content in dry samples of sea grass by this method was 25.8%.

All over the world, evaluations of the methods of obtaining cellulose have changed significantly. The strengthening of environmental requirements raised the question of the need to abandon technologies using sulfur and chlorine compounds already in the near future. To obtain cellulose from plant raw materials, two methods were chosen based on literature data [13].

Delignification of chopped wood was carried out in a glass reactor with a volume of 250 cm^3, equipped with a mechanical stirrer and a reflux condenser. A weight of raw material weighing 15 g was placed in the reactor and poured with the previously prepared reaction mixture.

The first method is proposed for processing flax fiber [14]. A solution of hydrogen peroxide is used as a reagent. Ammonium molybdate and sulfuric acid were used as catalysts. The concentration of hydrogen peroxide was 4%; the content of ammonium molybdate and sulfuric acid - 2.08 and 1.25%, respectively.

According to the second method, the treatment was carried out with a mixture of glacial acetic acid, hydrogen peroxide and distilled water, using sodium chromate as a catalyst. The method was developed by the authors of [12] for low-temperature delignification of wood. The optimal mode of the process: the mass fraction of "glacial" acetic acid in the cooking solution is 0.65; mass fraction of hydrogen peroxide (with conc. 30%) 0.35; catalyst concentration (sodium chromate) 0.0015 mol/dm^3, liquid modulus 10, temperature 80 °C, atmospheric pressure.

The optimal delignification time is 120 minutes. After that, the cellulose samples were separated from the solutions by filtration on a Buchner device under vacuum, washed with water until the reaction of the washing water was neutral, and dried to an air-dry state. The content of α-cellulose in the product was determined according to standard methods.

The decomposition of hydrogen peroxide under the influence of a catalyst is called a catalase process. It proceeds according to the scheme [13]

$$H_2O_2 + Cat \leftrightarrow M \rightarrow H_2O + 1/2\ O_2 + Cat \qquad 1$$

where M are peroxocomplexes of different composition. The most studied peroxocomplexes are based on molybdenum, tungsten and chromium.

The catalase process in the presence of organic acids is accompanied by the acylation of hydrogen peroxide with the formation of peracids.

$$H_2O_2 + Cat \leftrightarrow CatO + H_2O \quad 2$$

$$AcO + CatO \leftrightarrow Cat + AcOOH \quad 3$$

$$CatO \leftrightarrow M \rightarrow O_2 + Cat \quad 4$$

$$H_2O_2 + AcOH \leftrightarrow AcOOH + H_2O \quad 6$$

$$H_2O_2 \rightarrow H_2O + O_2 \quad 3$$

Here, the symbol CatO is used to denote a peroxo complex.

The formation of the peroxocomplex occurs according to scheme (2). The peroxocomplex oxidizes acetic acid according to reaction (3) with the formation of peracetic acid and regeneration of the catalyst. In parallel with this, the peroxocomplex is decomposed by reaction (4) with the release of molecular oxygen, while the catalyst is also regenerated.

Direct acylation of hydrogen peroxide with acetic acid is possible without the participation of a catalyst, according to reaction (5), but, of course, at a slower rate. The possibility of slow decomposition of hydrogen peroxide in reaction (6) without the participation of a catalyst should also be allowed.

During the laboratory experiment, the obtained cellulose samples were examined according to standard indicators, such as moisture content, ash content, and the total content of α-cellulose.

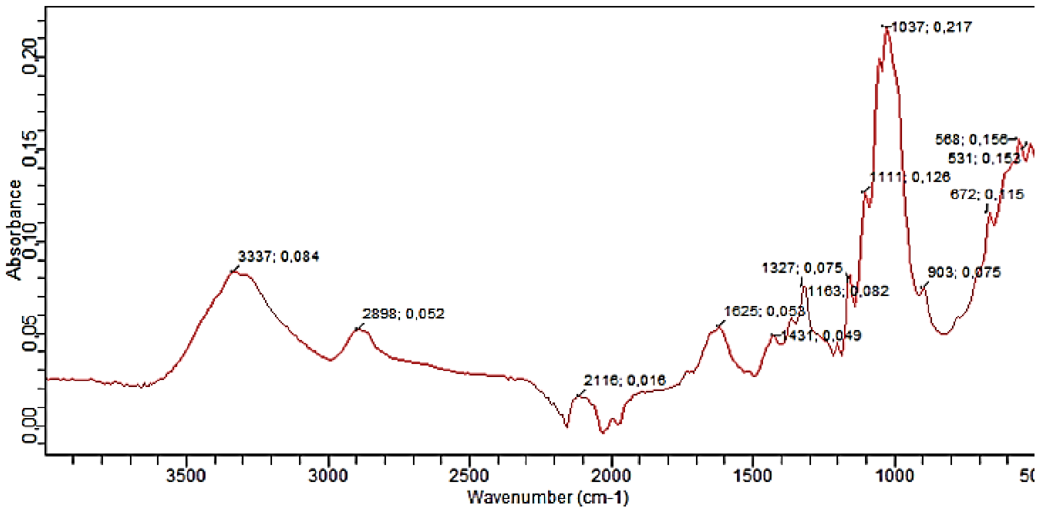
According to the research results, the following characteristics of cellulose samples were obtained: 1 – catalytic treatment with hydrogen peroxide, 2 – treatment in the presence of acetic acid.

Table 1. Indicators of cellulose samples

№	Time, hours	Output by mass, %	Content of α-cellulose, %	Ash content %
1	1	65,1	40,32	4,92
1	2	57,2	41,28	4,87
1	3	55,1	44,38	4,64
1	4	52,3	48,65	3,27
2	1	73,6	65,63	7,41
2	2	64,8	67,07	7,32
2	3	62,5	69,21	7,12
2	4	60,9	71,45	6,96

Cellulose samples obtained by two methods from vegetable raw materials were investigated by infrared spectroscopy.

The spectra are presented in Figure 7.



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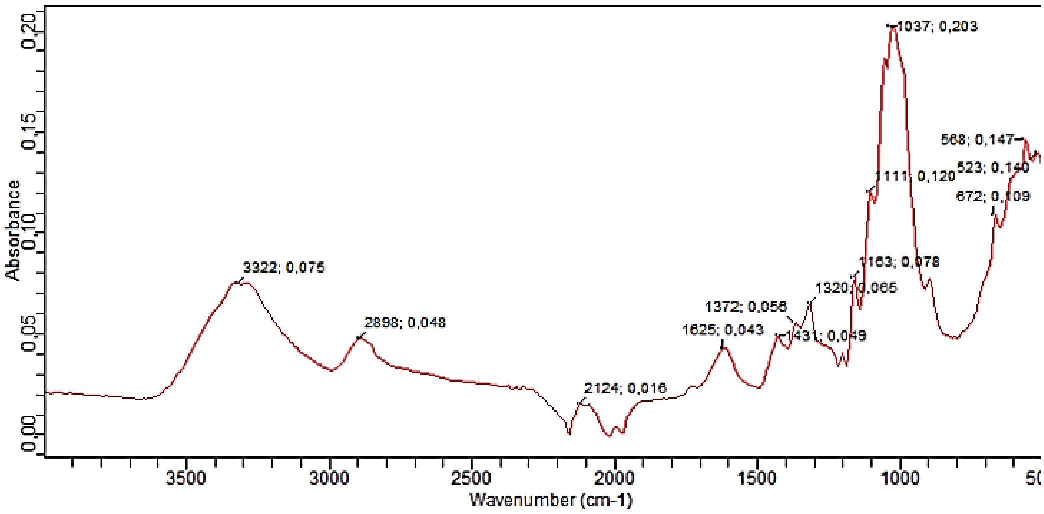

2

Figure 7 IR spectra of cellulose obtained by catalytic treatment of sea grass samples with hydrogen peroxide (1) and a mixture of hydrogen peroxide and acetic acid (2)

Conclusions. As can be seen from the above data, low-quality cellulose is formed at the optimal temperature for wood of 80°C. Of the two methods used in the work, the method of catalytic oxidation with peroxyacids gives a higher mass yield. Also, this method makes it possible to obtain a cellulose semi-finished product with an α-cellulose content of up to 71%. But under these conditions, the percentage of ash increases, which creates additional problems. Therefore, determining the optimal parameters of seagrass delignification requires further research.

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