Bark of Siberian Conifers

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Bark is successfully used as an innovative raw material to create effective environmentally friendly insulation materials. When using bark to obtain panels associated with tannin, the level of free formaldehyde is reduced. It is known that to increase the fire resistance of the composite, larch bark is mixed with clay.

softwood bark chemical composition extraction tanning extract tannin refinement ultrafiltration tan delignification biodegradation

1. Introduction

Forests are the dominant terrestrial ecosystem on Earth, accounting for 31% of the total land area [1]. The world's forested area is 4.06 billion hectares. Tree growing is the main task of forestry, as a result of which a large amount of renewable raw materials are produced annually. Most of the world's forests (54%) are located in the Russian Federation (815 million hectares), Brazil (497 million hectares), Canada (347 million hectares), the United States of America (310 million hectares), and China (220 million hectares), according to the data provided by the Food and Agriculture Organization of the United Nations (FAO) for 2020 [1].

The Krasnoyarsk Territory is 69.3% covered with forests and is one of the leading forested regions in the Russian Federation. The total forest resources of the Krasnoyarsk Territory amount to 164 million hectares [2]. The main forest-forming species in the Krasnoyarsk Territory are conifers; they occupy more than 75.9% of the forested area, which amounts to 9.7 billion m 3; the share of spruce and fir amounts to 16.0% (1.6 billion m 3) [3].

The most important feature of Siberian forests is the preservation of natural plantations in large areas that are relatively weakly exposed to human anthropogenic impact. Forest ecosystems have a natural (background) level of biodiversity and represent standards for population, species, and ecosystem diversity. These forests are fundamentally different from the "cultivated" forests represented in Western Europe and Russia by artificial plantations with reduced resistance to adverse environmental factors and climatic conditions [4].

Plant waste is a major source of environmental pollution. Millions of tonnes lay sitting in dumps for many years, creating additional pressure on the environment, as the bark decomposes slowly under natural conditions. In summer, bark dumps pose a fire hazard. In addition, dumping territories are excluded from the economic turnover. Burning the bark is not cost-effective due to its low heating value and its high ash and moisture content. It partially decomposes when stored for a long time, forming phenolic compounds, which are washed off by precipitation and meltwater. Pollution of the environment by these compounds can lead to disruption of the biological balance between individual links of biogeocenoses and thereby cause great damage to the national economy. At the same time, tree bark contains valuable extractives, and large-tonnage bark waste is a huge raw material resource for manufacturing expensive chemical products [5]. The problem of wood waste recycling is a weak point in integrated raw material processing [6][7][8][9].

2. Use of Coniferous Bark

Despite the high content of tanning substances in bark, barking waste from pulp and paper plants and wood processing plants is not used as raw material for tanning agents production due to the high content of wood impurities (up to 30%). This raw material composition leads to a decrease in quality of obtained extracts.

A modified type of bark is used for air purification as a biofilter, as well as for water purification, which allows for the binding of poisonous ions of lead, cadmium, mercury, and zinc [10].

In addition to the above, bark is a good lignin-carbohydrate complex that can be used as a sorbing agent for collecting oil products from the surface of polluted water bodies.

Bark can be used in new lignocellulosic composites [11]. Crushed bark is used as a filler in polylactic acid (PLA) composites, which have higher strength indicators and low moisture resistance compared to High Density Polyethylene (HDPE) composites [12]. In thermoplastic polymers, tree bark can be considered a filler, which leads to an increased heat capacity and thermal conductivity [13].

3. Chemical Composition of Coniferous Bark

The results presented in **Table 1** indicate that the chemical composition of larch bark differs markedly from other softwood bark. First of all, this refers to the content of water-extractable substances (as well as suberin and phenolic acids). The content of these components in larch bark is 1.5–3.0 times higher than in other types of softwood. At the same time, it has a low content of easily hydrolyzable polysaccharides, 1.5–2.0 times lower than others.

Table 1. Siberian softwood bark chemical composition [14][15][16][17][18].

Components	Content, % a.d.m. *			
	***Picea obovata* Ledeb**	***Larix sibirica* Ledeb**	***Pinus sylvestris* L.**	***Pinus sibirica* Du Tour**
Total ash	3.47	2.42	3.17	2.68
Extracted by hot water	4.58	11.80	6.30	4.92
Extracted by ethyl alcohol	2.54	8.30	5.25	7.13
Total extracted	7.22	20.10	11.55	12.06
Cellulose	26.40	22.90	27.30	25.00
König lignin	27.52	21.20	23.01	21.50
Easily hydrolyzable polysaccharides.	22.50	19.80	15.02	16.89
Hardly hydrolyzable polysaccharides	27.80	25.30	28.82	26.18

* Absolute dry raw matter.

Thus, bark contains a large number of elements that are necessary for tissue growth, with the exception of nitrogen and sometimes phosphorus.

The composition of extractive substances of the bark includes compounds of various classes: aliphatic and aromatic hydrocarbons, polyphenols, tannides, fatty acids, sterols, terpenoids, monosaccharides, pectin substances, and a number of other compounds.

The content of the main components in the bark of various types of larch is shown in **Table 2** .

Table 2. Group composition of larch bark of various types, % a.d.m. [19].

Components	Larch Bark		
	***Larix sibirica* Ledeb**	***Larix gmelinii* (Rupr.) Kuzen.**	***Larix kurilensis* Mayr**
Substances, extracted by:			
Hot water	11.80	18.73	21.50
Ethyl alcohol	8.30	-	-
Alcohol-benzene	3.90	11.40	10.90

Components	Larch Bark		
	Larix sibirica Ledeb	*Larix gmelinii* (Rupr.) Kuzen.	*Larix kurilensis* Mayr
Cellulose	22.90	19.40	18.80
Hexosans	6.10	-	-
Uronic acids	7.60	-	-
Pentosans (excluding uronic acids)	4.50	4.36	3.72
Klason lignin	41.66	36.12	37.40
Easily hydrolyzable polysaccharides	7.60	9.60	10.50
Hardly hydrolyzable polysaccharides	23.72	-	-
Ash substances	2.42	2.80	2.50
Methoxyl groups	5.35	1.42	1.60

4. Extraction Processing of Coniferous Bark

The table shows that fir, larch, and cedar bark is the richest in phenolic compounds. Larch bark is represented by almost all classes of flavonoids, from the flavanone naringenin to bioflavonoids, proanthocyanidins, and condensed tannins. The phenolic complex of larch bark is represented by phenolic acids and their esters; it contains monomeric flavonoids, spiroflavonoids, and oligomeric and polymeric flavonoid compounds.

According to previous studies, it has been established that Siberian larch bark is a great source of unique biologically active phenolic compounds, the quantitative content of which can reach up to 8–12% of absolute dry matter. The phytocomplex extracted from larch bark shows an antioxidant activity 1.5 times higher than dihydroquercetin [20]. Toxicopharmacological evaluation has shown that the antioxidant complex extracted from larch bark with ethyl acetate has a pronounced capillary-strengthening effect, which surpasses that of dihydroquercetin.

The main task for tanning substance extraction is the correct selection of an extraction agent that maximizes the substance extraction from the raw material.

The use of monoethanolamine as an additive to the main extraction agent makes it possible to extract from softwood bark, for example, larch bark, up to 50% of phenolic substances, which makes the obtained extracts promising for further processing [21].

5. Use of the Post-Extraction Residue

A result of the production of high-purity tanning extracts from softwood bark is a large-tonnage solid residue, the so-called tan, which has not found widespread use at present.

The chemical composition of the larch bark tan is given in **Table 3** [22][23].

Table 3. Chemical composition of tan bark *Larix sibirica* Ledeb, % a.d.m. [22][23].

Components	Content, % a.d.m.
Substances extracted by hot water	4.2
Easy-to-hydrolyze polysaccharides	15.3
Hard-to-hydrolyze polysaccharides	41.0
Cellulose	37.0
Lignin substances	46.1

Components	Content, % a.d.m.
Total ash	1.5

The results of **Table 3** show that the larch bark tan is represented mainly by polysaccharides and lignin. The share of polysaccharides accounts for up to 50%, the main portion of which is hard-to-hydrolyze polysaccharides. The polysaccharide content in the tan is higher than in the bark. Thus, the lignin content requires delignification in order to obtain a high-quality cellulose semi-product.

Thus, given the relatively high polysaccharide content, tan can be classified as a potential raw material for the production of cellulosic materials.

One of the ways to carry out delignification is oxidative destruction [23]. The main factors which have an impact on obtaining a product are the flow rate and concentration of hydrogen peroxide, the temperature and duration of processing, and the pH of the medium. The optimum parameters for the delignification of the larch bark tan are the following: temperature 80 °C, duration 2 h, hydrogen peroxide concentration 6%, and liquid module 10. The cellulose yield is up to 35% and the lignin content is 46%; thus, one treatment with hydrogen peroxide is not sufficient for a high-degree delignification. In this case, it becomes necessary to carry out a multi-stage delignification; one of the methods is bioconversion, in particular, by *Trichoderma* fungi. As a result of the conversion, lignin decreases to 21.4%, and cellulose enrichment is up to 48.2%. Application of the combined impact on the lignin-carbohydrate complex of the larch bark tan leads to an increase in cellulose; this is accompanied by lignin destruction. The resulting semi-product has a highly developed porous structure; this product is similar in its characteristics to powdered cellulose and can be used as a carrier for various biologically active substances [23].

In addition to oxidative destruction, tan can become a promising raw material for organosolv pulping in the acetic acid–hydrogen peroxide–water media, which has a number of advantages over traditional methods of cellulose pulping: toxic sulfur-containing compounds are excluded from the production cycle of cellulose pulping; the delignification process is carried out under mild conditions to obtain high-quality cellulose; the possibility of relatively low investment capital and ensuring the profitability of small and medium-sized enterprises [24].

The use of peroxy acid contributes to the production of bleached cellulose, which does not require additional processing. The spent pulping liquor can be reused (recycled) by adding fresh reagents and bringing them to a predetermined concentration [25]. The non-traditional pulping is an environmentally friendly method that does not require high temperature and pressure.

An alternative option is biotechnological processing—the transformation of some organic compounds of biological raw materials into others under the influence of enzymatic systems of microbial origin.

Various methods of bioconversion are used to regulate the phytopathogen population number and to obtain antimicrobial drugs; the dominant position is occupied by *Trichoderma* microscopic fungi which have a high antagonistic and superparasitic activity. It is known that *Trichoderma* fungi are able to actively participate in the destruction of lignin-cellulose waste from wood industry enterprises. The peculiarity of the fungus to decompose lignin substances along with cellulosic substances puts it in a number of agents capable of transforming plant raw materials of wood origin and allows for the potential to use this ability in the future to create a wood waste processing technology and to obtain bioproducts with a protective effect. The fungus' cellulolytic enzymes cannot penetrate the cellulose fibrils; they act only on the surface. The number of glycosidic bonds receptive to the effects of the enzymes depends on the cellulose's swelling degree. The increase in reactivity of cellulose depends on the grinding degree and the pretreatment of the raw material. The exposure to the effect of the enzyme complex is affected by the presence of inhibitors in the substrate, in particular, substances of phenolic origin [26].

Tan obtained as a result of larch bark treatment with alkali can be used as a substrate to obtain a biological product of the trichodermin type based on the strain MG-97 *T. asperellum* [27].

Larch bark extracts can be used as a modifying agent to obtain urea foam plastics [28] to improve strength characteristics.

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