Review

Bark of Siberian Conifers: Composition, Use, and Processing to Extract Tannin

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Abstract: The rational use of natural resources, including the creation of new and improvement of existing technologies in order to reduce the anthropogenic impact on the environment, is currently an important task. This review covers different methods of softwood bark processing. Bark is used for the production of heat-insulating plates, and also as filler in adhesives and composites. In agriculture, it is used as a mulch. Softwood bark is a valuable raw material for chemical processing. Extractive substances of the bark are of particular interest. Among them, phenolic compounds are very important, in particular of tannin nature, which are used as tanning agents in leather production. Bark is used for the isolation of substances with antibacterial activity for pharmaceutical and nutraceutical applications. Aqueous-alkaline solutions, in particular monoethanolamine, are used as an extracting agent. Currently, tannins have been applied into many different fields, including medicine, food, beverage, the manufacture of ink and adhesives, the dye and tanning industry, plastic resins, water purification, and surface coatings. Tanning extracts obtained as a result of extraction are refined by ultrafiltration. The obtained extracts are of high purity. The extraction residue, the so-called tan, is a promising raw material for obtaining a cellulosic product. In addition to the chemical conversion of tan, biotechnological processing is an alternative option. In the process of tan biodegradation by the microscopic *Trichoderma* fungus, a biological product trichodermin is obtained, which is used to protect plants from phytopathogens.

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

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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 m³; the share of spruce and fir amounts to 16.0% (1.6 billion m³) [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].

The annual conifer felling volume in the Krasnoyarsk Territory is 48.9 million m³. The total weight of wood used from the total volume of harvested wood is 75%. The share of bark is 6–15% and the share of foliage is 10–20%. The crown, a part of the trunk, top, twigs, stumps, roots, and some foliage are left in the felling area as logging waste. The amount of such waste varies from 30% to 50% of the total biomass [5,6].

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 [7]. The problem of wood waste recycling is a weak point in integrated raw material processing [8–11].

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.

Tree bark performs many functions during a plant's life: it preserves the cambium, covers the trunk, branches, and roots, thereby protecting against harmful microorganisms and preventing water loss, and also plays an important role in the event of fires [12–15]. Bark fire resistance depends on its thickness and moisture content. Bark anatomy depends on species, age, place of growth, and ecology [16].

Tree bark can be considered a biological indicator since, due to its porous structure, it is always subject to pollution from harmful air emissions [17–21]. It has been found that the quantitative content of phenolic compounds, waxes, tannins, and pectin substances in the Siberian and Dahurian larch bark is significantly affected by technogenic factors. The increased content of phenolic compounds is evidence of the development of plant defense mechanisms against growing conditions [22].

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 [23].

Bark can be considered a lignocellulosic waste [24] that can be recycled as a substrate for anaerobic fermentation.

Conifers are used to obtain biologically active polyphenols, in particular, dihydroquercetin and dihydrokaempferol products [25,26]. It is also possible to obtain a natural antioxidant complex based on phenolic compounds that has a number of properties, such as hepatoprotection, capillary protection, and antioxidant activity [27]. Currently, such complex is used as a biologically active additive (BAA) Picnolar. There is evidence for the ability to obtain pectins from larch bark, which are used in the food industry as a gelling agent, as well as in pharmaceuticals for removing radionuclides from the human body [28].

Bark is used to obtain substances with bactericidal and hydrophobic properties, such as wax, which is widely used in the cosmetic industry. Larch bark is used in traditional medicine as extracts that have diuretic properties, and ointments are used for healing wounds, as well as chronic eczema and psoriasis [29].

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.

Fir bark is used to obtain effective carbon sorbents using thermos-elastic activation in the presence of potassium hydroxide [30]. Enterosorbents obtained from crushed fir bark by treating it with a 1.5% aqueous solution of NaOH and hexane have good sorption properties [31]. The softwood bark post-extraction residue can be treated with modifiers, for example, the PMS-100 polymethylsiloxane liquid. At the same time, it has been found that the modified bark can retain hydrocarbon materials. The maximum hydrophobization efficiency was achieved for larch and pine bark [32].

Bark can be used in new lignocellulosic composites [33]. 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 [34]. In thermoplastic polymers, tree bark can be considered a filler, which leads to an increased heat capacity and thermal conductivity [35].

Bark is successfully used as an innovative raw material to create effective environmentally friendly insulation materials [36,37]. When using bark to obtain panels associated with tannin, the level of free formaldehyde is reduced [38,39]. It is known that to increase the fire resistance of the composite, larch bark is mixed with clay [40].

Bark water extracts can be successfully used in glue production. The hydroxyl groups of phenolic substances interact with formaldehyde and form a binding base, which is used for the production of waterproof chipboard and plywood [41,42].

The use of bark in agriculture for mulching reduces evaporation from the soil surface. Due to the mulch decomposition duration, soil needs less additional artificial fertilizers; it also contributes to aeration [43].

3. Chemical Composition of Coniferous Bark

Softwood bark is an abundant and inexpensive waste of the agro-industrial complex, which allows it to be used as a raw material for chemical processing. The relative volume of bark in the trunk for different species of conifers is as follows: larch 22–25%, pine 10–16%, spruce 6–13%, cedar 6–10%, and fir 11–19% [44]. With age, the relative volume of the crust decreases, and its thickness decreases in the direction from the rump to the top. Deterioration of growing conditions (excessive moisture or desiccation of soil, reduced light supply, etc.) leads to a decrease in the thickness of the crust [45–47]. The choice of processing methods is determined by the origin and amount of bark, its moisture content, composition, shape, and size of bark particles, as well as its storage and transportation conditions [48].

Table 1 provides the chemical composition of softwood bark [49–53].

Table 1. Siberian softwood bark chemical composition [49–53].

Components	Content, % a.d.m. *			
	<i>Picea obovata</i> Ledeb	<i>Larix sibirica</i> Ledeb	<i>Pinus sylvestris</i> L.	<i>Pinus sibirica</i> 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.

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.

Spruce bark differs from other softwood bark in its low content of extractive substances and, accordingly, in its higher content of easily hydrolyzable polysaccharides. The content of the latter in spruce bark is 1.5–2.0 times higher than in other softwoods. The differences in the content of cellulose and König lignin are less significant.

The cellulose content varies from 22.9% (larch) to 27.3% (pine). Spruce bark contains more König lignin, since its content reaches 27.5%, which is 4–6% more than in other softwoods. The larch bark differs because it not only contains less easily hydrolyzable polysaccharides, but also less König lignin and cellulose.

The data on the mineral components [54] indicate that the main cations in bark ash are calcium (0.6–0.8%), sodium (0.4–0.5%), and potassium (0.15–0.27%), which account for up to 60% of the total mineral substances. The content of other macroelements (magnesium (0.1–0.4%), iron (0.01–0.02%)) is low. Bark also contains so-called microelements: boron (up to 0.002%), manganese (0.02–0.05%), and copper (0.001–0.003%). Moreover, bark contains silicates; stone cells are especially rich in them. The most important anions in bark are phosphates (0.01–0.06%).

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

A review of the softwood bark chemical composition data showed that it differs significantly from timber in terms of the content of its main components and, perhaps most importantly, its high content of extractive substances, and this requires a different approach to choosing how to use and process bark.

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 extraction of substances is based on the method of isolating groups of extractive substances with different solubilities in organic solvents and water. In this case, the processing of the crushed bark is carried out with solvents in ascending order of their polarity.

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. [55].

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

The results of Table 2 indicate that the content of the main components is different in the bark of various types of larch. Siberian larch contains more cellulose and Klason

lignin and less extractive substances. It also differs significantly in the content of methoxyl groups [55].

The chemical composition of the main components of bark, bast, and cortex is varied. The thickness and quantitative ratio of the layers is different and depends on the age of a tree and the location of the bark along the trunk height. The physical properties of the layers are also very different. The outer cortical layer has 10 times less moisture than the bast layer. Tree bark is much richer in minerals than timber. It has been found that the ash contains macro- and microelements (Al (48–82%), Mn (25–43%), Mo (39–58%), Ca (40–63%), P (17–46%), Mg (24–44%), Zn (35–49%), Cu (13–26%), Fe (28–57%), B (21–57%), N (14–29%), K (25–39%), Ni (less than 1%), Cr (less than 1%), Pb (less than 1%), Si (less than 1%), and Na (25–39%)) [56–59]. Xylose (2.8–3.2%), arabinose (1.5–1.9%), and galactose (0.6–1.2%) are the main monosaccharides in bark that form hemicellulose.

Thus, the bark of the lower part of the trunk has a higher content of inorganic elements and carbon. The bark of lower part is characterized by increased content of ester-soluble substances (lipids), which is obviously associated with the accumulation of hoarding substances (acylglycerols) in old tissues. The content of water-soluble substances, including tannins and carbohydrates, decreases along the height of the trunk in the bast and increases in the bark. A similar picture is observed for alkali-soluble substances containing hemicelluloses and polyflavonoids. At the same time, an increased content of lignin in young bark tissues and cellulose in bark has been observed [60].

4. Extraction Processing of Coniferous Bark

Various types of extraction are used to recover components from plant raw materials by means of different extracting agents. Both polar and non-polar solvents can be used. The selection of the extracting agent depends on the nature of the extracted substance. The force field and hydrodynamic conditions have a significant effect on the intensity of the plant raw material extraction. The bark crushing process at the preparation stage for processing is quite important and by itself can determine the way in which this raw material will be used further. Grinding methods have a significant impact on the number of destroyed cells and the efficiency of the extraction process [61–63].

The use of different extracting agents allows biologically active complexes of polyphenolic compounds to be obtained from the bark; the complexes of polyphenolic compounds feature a quantitative predominance of certain fractions, as well as different physiological activities [64]. For example, in the methanol extract of larch bark, the dominant fraction is the oligomeric and polymer fraction of flavonoids. The oligomeric fraction consists of procyanidin and propelargonidin modules. Pyro-type biflavonoids are present in oligomeric and polymeric flavonoid compounds as structural links. Thus, oligomeric and polymeric flavonoids are the product of the condensation of flavan-3-ols [(–)-epiafzelechin, (+)-catechin, (–)-epicatechin] and spiro-type dimmers. Oligomeric and polymeric proanthocyanidins have a positive effect on the cardiovascular system (vasorelaxant activity) and are able to enhance capillary blood circulation (microcirculation), increasing capillary permeability, and have a high antiradical activity [65]. The results of studies carried out by a group of authors [66] showed that the studied softwood types contain a variety of biologically valuable compounds that have good potential for use in the pharmaceutical industry, as well as in agriculture and forestry. The yield of extractives recovered from softwood bark with ethyl acetate is shown in Table 3.

Table 3. Yield of softwood bark extractive substances, % a.d.m. [66].

Type of Softwood	Ethyl Acetate Extraction Yield (I)	Hexanoic Extraction Yield (II)	Phenolic Compound Yield of Extraction I	Water Extract Yield (III)
<i>Larix sibirica</i> Ledeb	8.65	0.69	92.0	4.75
<i>Abies sibirica</i> Ledeb	15.17	0.34	97.8	10.0
<i>Pinus sibirica</i> Du Tour	8.47	0.83	90.2	4.71
<i>Pinus sylvestris</i> L.	3.67	1.19	83.7	3.82
<i>Picea obovata</i> Ledeb	3.37	1.94	42.4	6.94

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.

Larch extracts have p-hydroxybenzoic, vinyl, *cis*-, *trans*-p-coumaric, *cis*-, *trans*-ferulic, protocatechuic, and caffeic acids, as well as *trans*-ferulates and *trans*-coumarates of higher aliphatic alcohols, mainly n-eicosanol [67,68]. Stilbenes found in bark are represented by resveratrol and astringenin, and stilbene glycosides are represented by piceid and *trans*-astringenin-3'-O- β -D-glucopyranoside [69]. A wide range of compounds is represented by a group of flavonoids: naringenin, eriodictyol, dihydrokaempferol, dihydroquercetin, kaempferol, quercetin, quercetin-3-O-arabinoside, quercetin-3-O-rhamnoside, (–)-epiafzelechin, (+)-catechin, (–)-epicatechin, larixinol, oligoflavonoids (procyanidins), and polymeric flavonoids (condensed tannins). For the first time, flavonoid compounds of the spiro type have been identified: spirobiflavonoids of larixidinol and larizinol, trimer—triflarixinol. Spirobiflavonoids are also involved in the formation of oligomeric and polymeric flavonoid compounds (condensed tannins) along with monomeric flavan-3-ols [70].

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 [71]. 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.

Twenty phenolic compounds have been identified in the ethyl acetate extracts of Siberian larch bark (*Larix sibirica* Ledeb.) and Gmelin larch bark (*Larix gmelinii* (Rupr.) Rupr.), which are represented by phenolic acids, flavonoids, and stilbenes. The predominant compounds in the bark of the studied species are compounds with a pyrocatechol type of aromatic ring substitution: *trans*-astringenin and its 3'-O- β -D-glucopyranoside, (+/–) catechin, quercetin, and its glycosides, and in the outer cortex (rhytidome), the greatest number of compounds have a p-hydroxyphenyl type of aromatic ring substitution. For the first time, quercetin-3-O- α -L-rhamnopyranoside has been found in larch bark. Stilbenes, the presence of which has been established in the bark, have not been found in the rhytidome, however, spirobiflavonoids are absent in the bark [72].

Studies of the quantitative and qualitative composition of phenolic compounds in Siberian spruce bark [73] have revealed that the main monomers and phenolic extractives of the bark are flavonoid dihydroquercetin, stilbene glycosides (isorapontin and astringin), and oligomeric and polymeric phenolic compounds. Flavonoid compounds from the mass of deresined ethyl acetate extract of spruce bark account for 17–18%, the content of stilbenes and stilbene glycosides accounts for up to 28–30%, and oligomeric and polymeric phenolic compounds account for about 15%. Oligomeric phenolic compounds of Siberian spruce bark consist of building blocks of stilbene glycosides, mainly represented by isorapontin and astringin. Phenolic extract is biologically active and has antioxidant, anti-inflammatory, antitumoral, and cardio- and neuroprotective properties.

Extractive substances of Siberian silver fir bark are represented by compounds of phenolic class. Aqueous extract of silver fir bark has higher biocidal activity against opportunistic and saprotrophic bacteria. The extract mainly contains quercetin, dihydroquercetin, and kaempferol compounds [74–76].

The presence of phenolic acids, as well as flavonoids (kaempferol, quercetin, dihydroquercetin) is characteristic of pine bark. The monomeric phenolic complex of the water-alkaline extract is mainly represented by phenolic acids.

The following phenolic acids were identified: *n*-oxybenzoic, *n*-coumaric, caffeic (3,4-dioxybenzoic), vanillic, ferulic, and simply catechic (3,4-dioxybenzoic) acid. *p*-coumaric and ferulic acids are represented by *cis*- and *trans*-isomers. The oligomers are mainly represented by condensed tannins [77–79].

The following compounds have been identified in the bark: phenolic acids, lignans, stilbene glycosides (resveratrol and pinostilbenoside), flavonoids (dihydroquercetin, catechin, and kaempferol glycosides), as well as dimeric and trimeric flavonoids (proanthocyanidins consisting of catechin and epicatechin structural models).

Pinosylvin, pinosylvin monomethyl ether, pinosylvin dimethyl ether, resveratrol, pinostilbene, resveratrol trimethyl ether, and stilbene glycosides such as resveratrol and pinostilbenoside have been found in cedar bark. These compounds are dominant among the phenolic extracts of bark. Phenolic acids, flavonoids (kaempferol, quercetin, and dihydroquercetin) are present in Siberian and Scots pine (*Pinus sylvestris* L.) bark. The biological activity of stilbenes has shown that pinostilbene, resveratrol, and astringenin display bacteriostatic, fungistatic, and tuberculostatic activity. Pinostilbene is highly active against human tubercle bacillus [80].

Among the phenolic compounds extracted from bark, the substances of tannin nature, which are used as tanning agents in leather production, are of the greatest interest. Tannins are complex polyatomic phenols; their molecule size and hydroxylation degree give them the ability to adequately dissolve in water and easily oxidize in alkaline solutions [81]. Tannins are usually soluble in alcohols, acetone, dioxane, and ethyl acetate if the solution contains at least a little water. In most cases, they are insoluble in ether, benzene, and similar solvents. They are mainly amorphous substances [82,83].

Despite the fact that synthetic tanning agents are widely used in the leather industry, tannins of natural origin have not lost their value. Leather products have a set of properties that are very difficult to reproduce in synthetic materials [84].

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

Tanning substances are almost completely recovered as a result of a water-alkaline extraction. The effect of alkaline solutions causes the hydrolysis of condensed structures. The highest yield of extractives from larch bark is observed when using 1–1.5% alkali water solution or 15–20% ethyl alcohol as an extraction agent. When using an alkali water solution, the yield of extractive substances is up to 40%, and the yield is 7–8% more when using a water-alcohol solution. The maximum yield of extractives from pine bark occurs when using a 2% sodium hydroxide solution.

Catechol, catechin, dihydroquercetin, quercetin, campherol, dihydromyricetin, and resveratrol have been identified in an alcohol extract of larch bark using a mass spectrometer [85].

The concentration of sodium hydroxide has a significant effect on the extraction efficiency, the results of studies indicate that when using a 1.5% NaOH solution, 2.5 times more substances are extracted than when using a 0.1% solution. This is due to the fact that structural changes of water under the influence of electrolytes, in particular NaOH, are significant only at moderate concentrations (from 0.2 to 2–3 mol/L). Among the available alkali metal hydroxides, NaOH is more effective, since it is better able to penetrate the capillary-porous structure of a substance [86].

Scientists of the Wood Chemical Engineering and Biotechnology Department, Reshetnev Siberian State University of Science and Technology, Krasnoyarsk, Russia, have con-

ducted research on the effect of extraction duration on the composition of water-alkaline extracts of Siberian larch. The bark has been preliminarily crushed to particles ranging from 0.5 to 1 mm in size; the extraction has been carried out with a 1% sodium hydroxide solution, the process temperature was 90 °C, the liquid module was 1/9, and the extraction duration was 35 min. According to the studies, the authors have established that the duration of a water-alkaline extraction process significantly affects the quality of the obtained extract, while the most complete extraction of tannins occurs from the raw material, and the processes of hydrolysis and condensation of tannins do not have a big effect on the quality of the extract obtained. The yield of a larch extract is at minimum 55%, and the purity is 43% [87–90].

One of the extraction methods is to use an organic ampholyte solvent as an additive to the main extraction agent—water. Monoethanolamine (MEA) has been chosen as an additive to water due to the following reasons. Firstly, MEA is a typical ampholyte and, therefore, its presence in the extraction agent facilitates transition to the liquid phase of substances of a different nature. Secondly, being an antioxidant and a weak destructive agent for lignin [91], MEA is able to prevent oxidative processes, as well as to inhibit the condensation of polyphenolic compounds and ensure the preservation of the carbohydrate complex [92]. Thirdly, when using MEA, the rate and completeness of extractive substance recovery may be increased, since this solvent is a good swelling agent for plant raw materials [93]. Apart from monoethanolamine, other ampholytes also have the same properties [94].

The use of monoethanolamine as an additive to the main extraction agent (water) in the amount of 1.0% to 5.0% allows for the extraction of 28% to 58% of low molecular weight substances from softwood bark, including a certain amount of easy-to-hydrolyze polysaccharides (6.8–19.0% of extract dry matter mass), while with other ways of extractive substance recovery, the maximum yield has been about 24% with 12.3% of total concentration of organic solvents in the extraction agent [95].

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 [96].

Extraction products obtained using monoethanolamine have antimicrobial properties, in some cases with prolonged action, which are provided by phenolic compounds [97].

There is a method of obtaining tanning extracts with a preliminary short-term bark activation, followed by extraction using a water-alcohol solution [98]. This method allows the yield of tannins to be increased.

The presence of a significant amount of substances that do not have the tanning effect in softwood bark extracts reduces the extract quality and limits their use. This is especially applicable to alkaline extracts from softwood timber barking residues, in which the content of tanning substances is less than 40%. Tanning extracts are refined in order to improve the quality of the obtained plant extracts. The most effective methods for refining alkaline extracts are neutralization with an ion exchange resin, sulfitation, and ultrafiltration.

The extract study results have revealed that non-tannins have a molecular mass 400–1000 less than that of tannins (i.e., the difference in the molecular mass between them is very significant), and this, in turn, makes it possible to refine extracts by means of ultrafiltration. This method allows extracts to be obtained with a defined level of quality regardless of the bark composition at the stage of tanning extract refinement and, thereby, helps solve the problem of wood waste recycling. Ultrafiltration is a delicate hydromechanical process. The main driving force behind the process is a pressure difference on both sides of the membrane.

Depending on the purpose of the process, semi-permeable membranes with pore sizes from 5×10^{-9} to 5×10^{-8} m and porosity of $\approx 80\%$ are used for ultrafiltration. Ultrafiltration separation of mixtures is carried out using four main types of membranes: the asymmetric Loeb-Sourirajan membranes, composite membranes, nuclear filters, and hollow fibers. Semi-permeable membranes in the form of hollow fibers have an asymmetric

structure. The main advantage of hollow fibers is a larger surface area of the membranes per unit volume of the appliance. The high packing density of fibers in the membrane module ensures the high performance of hollow fiber appliances.

During the ultrafiltration of tanning solutions, they are concentrated and purified from mineral salts and other low molecular weight impurities, which pass into the permeate (filtrate). At the same time, high-molecular tannins remain in the concentrate (the solution above the membrane), and the solution purity increases significantly. The optimum conditions for this ultrafiltration process are as follows: pressure of 400 kPa, temperature of the fractionated spent tanning solution of 35 °C max., and pH value of 4–5 [99–101]. An increase in temperature above 35 °C causes the disaggregation of colloidal particles and increases their mobility. In this case, the ratio of solution components changes towards highly dispersed components, which contributes to the penetration of tannins into the filtrate, and the concentrate purity decreases. A decrease in the acidity of the fractionated tanning solution from pH 4 to pH 6, just like an increase in temperature, disaggregates the colloidal associates of tannins, which negatively affects the selectivity and productivity of the ultrafiltration process.

The results of Table 4 show that the highest yield of tannides is observed using a hollow fiber ultrafiltration acetate cellulose membrane with a pore size of 10 micrometers (UMAC-HF10*).

Table 4. Influence of membrane type on the tannin yield of aqueous-alkaline extract of *Larix sibirica* Ledeb bark, % a.d.m. [89].

Name of the Fraction	Content of Substances, % a.d.m.						
Type of Membrane	HMAC-50 ^a	HMAC-80	UMAC-HF10 ^b	UMAC-HF10 *	UMAC-50 ^c	UMAC-100	UMAC-500
Concentrate	96.2	97.1	95.3	95.8	93.6	96.3	96.3
Filtrate	1.4	0.3	0.3	0.7	3.6	1.0	3.7
Precipitate on the membrane	2.4	2.6	4.4	3.5	2.8	2.7	-
Tannin yield (concentrate + filtrate)	$\frac{43.9}{81.2}$	$\frac{34.7}{74.7}$	$\frac{82.4}{187.9}$	$\frac{74.8}{170.6}$	$\frac{74.3}{156.8}$	$\frac{48.2}{112.9}$	$\frac{34.4}{76.1}$

The numerator is the percentage of original extract dry matter, the denominator is the percentage of tannins in the extract.

^a Hyperfiltration membrane acetate cellulose. ^b Ultrafiltration membrane acetate cellulose—hollow fiber. ^c Ultrafiltration membrane acetate cellulose. *—the volume of the selected filtrate was 25%.

Another promising raw material for obtaining tanning substances is pine bark. Studies of the bark chemical composition [102–105] indicate that it is a valuable raw material for chemical processing.

The results given in Table 5 show that pine bark is a complex of substances, consisting of extractives, polysaccharides, and lignin. Extractive substances are of the greatest interest. The maximum recovery of extractives is achieved with 2% NaOH. The yield of substances extracted with alkali is 6 times more than water-soluble substances and 1.5 times more than alcohol-soluble substances; after a neutralization on a cation exchange resin KU-2, pine bark already has a high purity reaching more than 60%. The research results are given in Table 6.

Table 5. Chemical composition of the bark of *Pinus sylvestris* L. [106].

Components	Content, % a.d.m.
Total ash	3.2 ± 1.3
Substances extracted by hot water	7.2 ± 2.4
Substances extracted with 2% sodium hydroxide	44.0 ± 4.1
Substances extracted by ethyl alcohol	31.6 ± 4.5
Easily hydrolyzable polysaccharides	13.4 ± 3.2
Hardly hydrolyzable polysaccharides	27.8 ± 4.4
Lignin substances	43.0 ± 3.7

Table 6. Purification extract bark of *Pinus sylvestris* L. [106].

Extract Refining Stages	Purity, %
Neutralization with a cation exchange resin KU-2	68.4 ± 3.0
Treatment with sodium sulfite	70.6 ± 3.2
Ultrafiltration, concentration 25%	65.2 ± 5.0

Thus, a water-alkaline extract of pine bark does not require additional refinement by ultrafiltration; it is sufficient only to neutralize the extract on the KU-2 resin and modify it by sulfitation [106].

The water-alkaline extract is mostly represented by polyphenolic compounds, a significant part of which has tanning properties, according to the results of tannin determination as per the All-Union Standard Method (VEM, 1953).

Since the production of hide powder, a sorbent used in the VEM method, has been currently stopped, the method has been modified, and collagen is used as a sorbent substance, which is very similar in structure to hide powder [107]. The research results given in Table 7 show that the extract composition is represented by more than 60% by substances of tannin nature, the purity of this extract is at minimum 61%.

Table 7. Composition of aqueous-alkaline extract bark of *Pinus sylvestris* L. [107].

Component	Content	
	VEM Collagen Method	VEM Hide Powder Method
Dry substances, g/L	23.5	
Insoluble substances, %	1.3	2.1
Soluble substances, %	98.7	97.9
Non-tannins, %	36.7	40.0
Tannins, %;	63.3	60.0
Purity, %	64.1	61.3

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 8 [108,109].

Table 8. Chemical composition of tan bark *Larix sibirica* Ledeb, % a.d.m. [108,109].

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
Total ash	1.5

The results of Table 8 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 [109]. 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 [109].

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 [110].

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 [111]. 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 [112].

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* [113].

Larch bark extracts can be used as a modifying agent to obtain urea foam plastics [114] to improve strength characteristics.

6. Conclusions

Wood waste is a potentially important source of raw materials. Waste is generated as a by-product during the harvesting and processing of wood around the world. Therefore, the use of bark is of exceptional importance because of its unique chemical components and unusual structure.

The conducted search and study of literary sources has included a general overview of the chemical composition of bark and bark processing. Special attention was drawn to extractive substances of the bark, among which phenolic compounds with biological

activity and tanning ability are important. Although synthetic tanning agents are widely used in the leather industry, tannides of natural origin have not lost their significance.

In the tanning and extract industry, the extracts obtained have a low yield and good quality, which generates interest in further studying this problem.

In the production of tanning extracts, a multi-tonnage waste is a post-extraction residue, the so-called tan, which has not yet found a qualified application.

The review has covered the ways of tree bark processing that allow its products to be used in various industries.

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