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(54) **METHOD OF PREPARING CELLULOSE NANO-FIBRES FROM STALKS OF ANNUAL PLANTS**

VERFAHREN ZUR HERSTELLUNG VON NANOFASERN AUS DEN STÄNGELN VON EINJÄHRIGEN
PFLANZEN

PROCÉDÉ DE PRÉPARATION DE NANO-FIBRES DE CELLULOSE À PARTIR DE TIGES DE
PLANTES ANNUELLES

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Description

[0001] This invention relates to the preparation of cellulose nano-fibres from stalks of annual crops.

[0002] From the patent application US 20080146701 a method is known of preparing cellulose nano-fibers from a fibrous pulp derived from natural fibers, root crops, fibre crops which contain hemicellulose, lignin, pectin and mineral substance. The method comprises several consecutive steps of preparing the nano-fibres: hydrolysis of the fibrous pulp by means of a diluted acid at temperature of 70 - 90°C, extraction in alkaline medium, cryogenic disintegration, and defibrillation in a homogenizer at high pressure. The obtained nano-fibers may be used as reinforcement in resin composites prepared by film casting, forming or extrusion for application in medical devices and packaging.

[0003] From the patent description EP 2 415 821 known is a method of preparing a cellulose gel. The method consists in that the cellulose material is first treated with an oxidizing agent generating carboxylic groups on the cellulose surface. The suspension of the cellulose material is then homogenized and the obtained suspension of nano-fibers is treated with an organic-or inorganic acid to cause the cellulose nano-fibers aggregate into a gel. In order to solidify the gel, it is subjected to UV irradiation or to the action of a cellulase preparation or ozone and peroxides. The liquid gel is again mechanically processed. The outcome is a gel which contains cellulose nano-fibres holding free carboxylic groups on its surface. The prepared cellulose gel reveals low water absorption and swelling due to that the unreacted carboxylic groups are not as prone to dissociation as those reacted to salts.

[0004] Patent US 8546558 describes a method of preparing micro-fibril cellulose from a hemicellulose-containing sulfite pulp derived preferably from coniferous wood. The method involves mechanical grinding, action of hemicellulase or cellulase or mixture of the two and a further mechanical homogenization. Prospective uses of the micro-fibril cellulose are in food, cosmetics, pharmacy, paper, composites, coatings and thickeners.

[0005] A method to make cellulose nano-fibrils is described in the international patent application WO 2010092239. The method provides preparation of a suspension of cellulose fibers upon which adsorbed is a cellulose derivative (e.g. carboxymethylcellulose) or a polysaccharide or its derivative. The fibers are then disintegrated to nano-fibrils. Chemical-, mechanical-, thermo-mechanical or chemical-thermo-mechanical cellulose pulp was used as starting material. It was derived from wood, non-woody materials or recycled cellulose fibers. The nano-fibrils sized below 1 micrometer find their uses in food, concrete, drilling fluids, coatings, cosmetics, drugs and paper.

[0006] Known from the international patent application WO 2013188657 is a method for the manufacture of nano-fibres from a cellulosic material by processing of an aqueous suspension with a cellulose depolymerizing

agent such as ozone, cellulase or a combination of the two, and a parallel or subsequent mechanical disintegration which delivers nano-fibers from the cellulosic material. Low energy consumption is an asset of the method in comparison to processes employing only mechanical disintegration. Nano fibers from the method find their use in paper making.

[0007] The method of preparing cellulose nano-fibers from stalks of annual plants according to the invention consist in that the stalks cut into pieces 10-70 mm long are processed in following steps:

- a) action of water vapor at 1,5-3 bar for 5-60 minutes
- b) mechanical defibrillation in a disk mill for 3-10 minutes
- c) digestion in a digesting liquor containing 5-15wt% of NaOH on dry mass of the stalks; liquor module from 3:1 to 8:1, time 60 to 120 minutes, temperature 110-160°C
- d) delignification with oxygen in a medium containing 2-4wt% of NaOH and 0,2-0,5wt% of MgSO₄ on dry mass of the stalks. Conditions: oxygen pressure at start 0,2 - 0,5 MPa, pulp concentration 8-15wt.%, time 60 - 120 minutes, temperature 110 - 120°C
- e) bleaching at least twice with NaClO₂ at concentration of 1 - 1,5wt.% and H₂SO₄ concentration of 0,05 - 0,1wt.% at 60 - 70°C for 60-120 minutes, followed by alkaline extraction in aqueous NaOH with concentration of 0,5 - 1wt% at 70 - 80°C, for 60-120 minutes
- f) enzymatic treatment of the prepared cellulose pulp by cellulase at activity of endo-1,4-beta-glucanase of 10-1000 J/g on dry mass ; pH of 4-7, temperature 40 - 60°C, time 30-480 minutes, agitation-50 - 500 followed by washing of the cellulose pulp with demi water, and vacuum filtration, and deactivation of the residual enzyme in the pulp at 90 - 125°C, for 10 - 30minutes
- g) homogenizing of the aqueous cellulose suspension with concentration of 0,5 - 3 wt%, at 5000 - 20000 rpm for 1 - 10 minutes, wherein during the agitation, the suspension is quenched with refrigeration brine at about -15°C, wherein next the suspension is centrifuged at 4000 - 15000 rpm for 5-30 minutes to obtain a supernatant containing cellulose nano-fibres.

[0008] The digesting in step c) can, according to the invention, be run in a liquor with a content on dry mass of 5 - 15 wt.% of NaOH and 0,1 - 0,5 wt.% of anthraquinone or a liquor with 5 - 15 wt% of NaOH, 3 - 6 wt% of H₂O₂, 0,1 - 0,3 wt% of ethylenediaminetetraacetic acid (EDTA), 0,2 - 0,5 wt% of MgSO₄ and 2 - 5 wt% of water glass.

[0009] The cellulose pulp is, according to the invention, in addition to the bleaching in step e) preferably put to de-lignification by the action of 1 - 2 wt% of peracetic acid and 0,2 - 0,5 wt% of MgSO₄, calculated on dry mass.

Conditions: temperature of 80 - 90°C for 60-120 minutes.

[0010] The cellulose pulp holding about 50 - 70 wt% of water is, after the bleaching in step e) and prior to the enzymatic treatment in step f), preferably put for 20 - 90 minutes to mechanical defibrillation followed by homogenizing in water suspension.

[0011] According to the invention, the sediment formed after homogenization and centrifugation in step g) can be recirculated to step f) and put to repeated enzymatic treatment with a solution of cellulase.

[0012] The multi-stage de-lignification combined with bleaching of the lingo-cellulose raw material, according to the invention, offers the chance of removing the non-cellulosic substance without a far-going degradation of cellulose thus providing a high output of cellulose pulp with excellent purity. Moreover, the multi-stage mechanical treatment of the pulp combined with enzymatic hydrolysis of cellulose makes it possible to prepare cellulose nano-fibres having a high proportion of length to thickness. The method according to the invention enables the utilization of agriculture residues such as linen and hemp waste straw remaining after the separation of seeds for oil expression.

[0013] The nano-fibres made according to the invention can be used as reinforcement in the production of composite materials, as thickener or constituent of a variety of coatings

[0014] The invention is illustrated with following embodiments which should not be construed as limiting the invention in any manner.

Example 1

[0015] Hemp stalks cut to pieces 40 - 60 long were loaded into a 15 dm³ swing digester and put for 10 minutes to the action of 2 bar steam and then three times defibrillated in the disk mill of Sprout-Waldron type with a consecutive decrease of the distance between the defibrillating elements (0,5, 0,2 and 0,1 mm). The slackened plant raw material was for 60 minutes digested at 110°C in a liquor containing: 5 wt.% of NaOH, 5,5 wt.% of H₂O₂, 0,3 wt. of EDTA, 0,5wt.% of MgSO₄ and 5% water glass calculated on dry mass at fluid module of 4:1.

[0016] The fibrous pulp was subjected to delignification with oxygen in a medium containing 2,5 wt% of NaOH and 0,5 wt% of MgSO₄ on dry mass with oxygen pressure at start of 0,2 MPa, pulp concentration 8wt%, for 60 minutes, at 120°C. After the delignification, the cellulose pulp was bleached twice with sodium chlorite at NaClO₂ concentration of 1,4wt% and H₂SO₄ concentration of 0,1wt% at 70°C, for 120 minutes. After every chemical treatment, the cellulose pulp was washed with demi water and centrifuged. The prepared cellulose pulp was characterized by lignin content of 0,45% and alfa-cellulose content of 85,5 wt%, and average polymerization degree of 1266. Total output of the process was 65,9%. An aqueous 2,5 wt% suspension of the cellulose in a conical flask was placed on the platform of incubator with a rotation shaker

Labfors (Infors) and put to enzymatic treatment with cellulase (Ecostone L900, AB Enzymes) having endo-1,4-beta-glucanase activity of 500 J/g at pH of 4.8 at 50°C, for 180 minutes at agitation rate of 150 rpm. The processing finished and cellulose filtered on a Büchner funnel with filtration paper, the residual enzyme in the cellulose pulp was deactivated in an autoclave at 121°C, for 20 minutes. The 1.5wt% aqueous suspension was for 10 minutes homogenized in the homogenizer Ultra Turrax T50 (IKA) at 10000 rpm. During the homogenization, the suspension was quenched with refrigerating brine at -15°C. Homogenization finished, the suspension was for 20 minutes centrifuged on centrifuge Rotina 420 at 4500 rpm to separate the cellulose- - nano-fibers- containing supernatant.

[0017] The prepared fibers were characterized by thickness in the range of 30 to 120 nm and average molecular degree of 130.

Example 2

[0018] Stalks of fire type flax cut to pieces 30 - 50 mm long were steam-processed and defibrillated as in Example 1 and, then, for 60 minutes at 160°C digested in a liquor containing 15wt.% of NaOH and 0,1wt% of anthraquinone at fluid module of 7:1. Delignification, bleaching with sodium chlorite and alkaline extraction were carried out like in Example 1. The cellulose pulp was again put for 120 minutes at 80°C to delignification in a solution containing peracetic acid at concentration of 2 wt% and MgSO₄ at concentration of 0,5wt%. The obtained material was washed with demi water and centrifuged. The prepared cellulose pulp was characterized by lignin content of 9 wt% and alfa-cellulose content of 80,3 wt%, and average polymerization degree of 1306. Total output of the process was 69,5%. The cellulose pulp was put to mechanical treatment for 60 minutes at 40 rpm in a laboratory shredder. The 1,5wt% aqueous suspension of cellulose was put to enzymatic treatment like in Example 1 save amount of enzyme which was 300 J/g. The residual enzyme in the cellulose pulp was deactivated like in Example 1. The 1,5wt.% aqueous suspension of cellulose was homogenized by means of the homogenizer Ultra Turrax T50 in 3 cycles with the G45F tool and 3 cycles with W65SK tool at 10 000 rpm for 3 minutes in each of the cycles. During the homogenization, the suspension was quenched with refrigerating brine at about -15°C. The cellulose suspension was centrifuged as in Example 1 and the cellulose- -nano-fibers- containing supernatant was separated. The prepared fibers were characterized by thickness in the range of 40 to 160 nm and average molecular degree of 155.

Example 3

[0019] Stalks of oil flax cut to 30 - 60 mm pieces were steam-treated, defibrillated, digested, put to delignification in oxygen medium, bleached with sodium chlorite

and alkaline-extracted like in Example 1. The prepared cellulose pulp was characterized by lignin content of 14 wt% and alfa-cellulose content of 72,4 wt%, and average polymerization degree of 1151. Total output of the process was 92,3%. The cellulose pulp was enzyme-treated like in Example 1. A 2,5 wt% suspension of the cellulose in water was next prepared and put to homogenization in the homogenizer Ultra Turrax T50 at 10 000 rpm for 3 minutes in each of the 5 homogenization cycles. During the homogenization, the suspension was quenched with refrigerating brine at about -15°C. The cellulose suspension was thereafter for 20 minutes centrifuged at 4 500 rpm. After the separation of the supernatant, the deposit was again put to enzyme treatment like in Example 1, employing cellulase with endo-1,4-beta-glucanase activity of 200 J/g. From the remaining sediment prepared was a 1,5 wt% cellulose suspension in demi water which was for 3 minutes mechanically processed in each of the 3 cycles by means of the homogenizer Ultra Turrax T50 at 10 000rpm. The suspension was in the consecutive step for 20 minutes centrifuged at 4 500 rpm. Supernatants from both steps of the processing were combined thus improving the output of the process. The prepared fibers were characterized by thickness in the range of 45 to 200 nm and average molecular degree of 190.

Claims

1. Method of manufacturing cellulose nano-fibres from stalks of annual plants **characterized by** that pieces of annual plants stalks 10-70 mm long are subjected to processing in following steps:

- a) action of water steam at pressure of 1,5 - 3 bar during 5-60 minutes
- b) mechanical defibrillation for 3 to 10 minutes in a disk mill
- c) digestion for 60 to 120 minutes at temperature of from 110 to 160°C in a pulping liquor with 5 -15 wt% content of NaOH calculated on dry mass of the stalks, at liquid module of from 3:1 to 8:1
- d) oxygen delignification in aqueous medium containing 2 - 4 wt% of NaOH and 0,2 - 0,5 wt% of MgSO₄, on dry mass; process conditions: oxygen pressure at start 0,2 - 0,5 MPa, concentration of mass 8 -15wt% wag., time 60 - 120 minutes, temperature 110 - 120°C
- e) bleaching, at least twice, with sodium chlorite at NaClO₂ concentration of 1 - 1,5wt% and H₂SO₄ concentration of 0,05 - 0,1wt% at temperature of 60 - 70°C for 60-120 minutes, followed by alkaline extraction in aqueous NaOH with concentration of 0,5 - 1wt% at temperature of 70 - 80°C for 60-120 minutes
- f) enzymatic treatment of the prepared cellulose pulp with cellulase at activity of endo-1,4-beta-

glucanase of 10-1000 J/g on dry mass, at pH of 4 - 7, at temperature of 40 - 60°C, for 30-480 minutes, with agitation of 50 - 500 rpm followed by washing of the cellulose pulp with demi water, and vacuum filtration, and deactivation of the enzyme residual in the pulp at temperature of 90 - 125°C for 10 - 30minutes

g) homogenizing of the aqueous cellulose suspension with concentration of 0.5-3wt%, at agitation speed of 5000 - 20000 rpm for 1 - 10 minutes, wherein during the agitation, the suspension is quenched with refrigeration brine at about -15°C, wherein next the suspension is centrifuged at 4000 - 15000 rpm for 5 - 30 minutes to obtain a supernatant containing cellulose nano-fibres.

2. Method according to Claim 1 **characterized in that** the digesting liquor contains 0,1 wt% of anthraquinone.
3. Method according to Claim 1 **characterized in that** the digesting liquor contains 3 - 6 wt% of H₂O₂, 0,1 - 0,3 wt% of ethylenediaminetetraacetic acid (EDTA), 0,2 - 0,5 wt% of MgSO₄ and 2 - 5 wt% of water glass.
4. Method according to Claim 1 **characterized in that** the cellulose pulp after step e) is put to one more delignification with peracetic acid at concentration of 1 - 2 wt% and a 0,2 - 0,5 wt% concentration of MgSO₄, in proportion to dry mass, at temperature of 80 - 90°C, for 60-120 minutes.
5. Method according to Claim 1 **characterized in that** that the cellulose pulp with moisture content of 50 - 70% after the bleaching in step e), is prior to the enzymatic treatment in step f) put to mechanical defibrillation for 20 - 90 minutes followed by homogenizing in aqueous suspension.
6. Method according to Claim 1 or 2 or 3 **characterized in that** that the sediment remaining after homogenization and centrifugation in step g) is recirculated to step e).

Patentansprüche

1. Art und Weise der Herstellung von Zellulose-Nanofasern aus den Stängeln der einjährigen Pflanzen charakterisiert sich dadurch, dass die 10-70 mm langen Fragmente der Stängel der einjährigen Pflanzen in folgenden Etappen bearbeitet werden:

- a) Behandlung mittels des Wasserdampfs unter dem Druck von 1,5-3 bar innerhalb von 5-60 Min.;

- b) mechanische Zerfaserung in einer Scheibenmühle innerhalb von 3-10 Min.;
- c) Beuchen in der Flüssigkeit, die 5-15% NaOH im Verhältnis zur trockenen Stängelmasse enthält, Flüssigkeitsmodul 3:1-8:1, innerhalb von 60-120 Min., Temperatur 110-160°C;
- d) Delignifizierung im Sauerstoffumfeld mittels wässriger Lösung, die 2-4% NaOH und 0,2-0,5% MgSO₄ enthält, im Verhältnis zur trockenen Masse, Anfangsdruck des Sauerstoffs von 0,2 - 0,5 MPa, Konzentration der Masse 8-15%, innerhalb von 60 - 120 Min., Temperatur 110 - 120°C;
- e) mindestens zweimaliges Bleichen mittels des Natriumchlorits bei NaClO₂-Konzentration von 1 - 1,5% und H₂SO₄-Konzentration von 0,05 - 0,1%, Temperatur 60 - 70°C, innerhalb von 60 - 120 Min. und die darauf nachfolgende alkalische Extraktion in der NaOH-Lösung von der Konzentration 0,5 - 1%, Temperatur 70 - 80°C, innerhalb von 60-120 Min.;
- f) enzymatische Behandlung erhaltener Zellulosemasse mittels der Zellulase von der Aktivität Endo-1,4-beta-Glukanase von 10-1000 J/g, im Verhältnis zur trockenen Masse, bei pH-Wert von 4 - 7, Temperatur 40 - 60°C, innerhalb von 30-480 Min., bei Mischgeschwindigkeit 50 - 500 U/min., danach Waschen der Zellulosemasse mittels des enthärteten Wassers und Abfiltrieren unter vermindertem Druck, danach Desaktivierung des in der Zellulosemasse übrig gebliebenen Enzyms bei der Temperatur 90 - 125°C, innerhalb von 10 - 30 Min.;
- g) Homogenisierung der wässrigen Zellulose-Suspension von der 0,5-3%-Konzentration mit der Drehgeschwindigkeit von 5000 - 20000 U/min., innerhalb von 1 - 10 Min., abgekühlt während der Homogenisierung mittels der Sole von der Temperatur ca. - 15°C, danach Zentrifugieren der Suspension bei der Drehgeschwindigkeit von 4000 - 15000 U/min. innerhalb von 5 - 30 Min., um den die Zellulose-Nanofasern enthaltenden Supernatant zu erzielen
2. Art und Weise gemäß Vorbehalt 1 charakterisiert sich dadurch, dass die Beuchen-Flüssigkeit 0,1% Antrachinon enthält.
3. Art und Weise gemäß Vorbehalt 1 charakterisiert sich dadurch, dass die Beuchen-Flüssigkeit 3 - 6% H₂O₂, 0,1 - 0,3% Versensäure, 0,2 - 0,5% MgSO₄ und 2 - 5% Wasserglas enthält.
4. Art und Weise gemäß Vorbehalt 1 charakterisiert sich dadurch, dass die Zellulosemasse nach dem Beuchen in der Etappe e) mit der zusätzlichen Delignifizierung mittels der Überessigsäure von der Konzentration 1 - 2% der Überessigsäure und 0,2 - 0,5% MgSO₄, im Verhältnis zur trockenen Masse, Temperatur 80 - 90°C, innerhalb von 60-120 Min. behandelt wird.
5. Art und Weise gemäß Vorbehalt 1 charakterisiert sich dadurch, dass die Zellulosemasse von der Feuchtigkeit 50 - 70% nach dem Beuchen in der Etappe e) vor der enzymatischen Behandlung in der Etappe f) mit der mechanischen Zerfaserung innerhalb von 20 - 90 Min. und danach der Homogenisierung in der wässrigen Suspension behandelt wird.
6. Art und Weise gemäß Vorbehalt 1 oder 2 oder 3 charakterisiert sich dadurch, dass der nach der Homogenisierung und Zentrifugierung in der Etappe g) entstandene Schlamm zurück in die Etappe e) zugeführt wird.
- ## Revendications
1. La méthode de production de nano - fibres celluloses des tiges des plantes annuelles se **caractérise par** cela, que les tranches des tiges des plantes annuels de la longueur 10-70 sont soumis au traitement dans les étapes suivantes :
- a) action par vapeur d'eau sous pression de 1,5 - 3 bars pendant 5-60 minutes.;
- b) défibrage mécanique dans le moulin à disques pendant 3-10 minutes ;
- c) digestion dans le liquide de digestion contenant 5-15% du poids de NaOH par rapport à la masse sec des tiges, avec le module de la liquide 3:1-8:1, pendant 60-120 minutes, dans la température de 110-160°C ;
- d) délignification dans l'environnement de l'oxygène de l'eau par la solution contenant 2-4% du poids de NaOH et 0,2-0,5% du poids de MgSO₄, par rapport à la masse sec, avec la pression initiale d'oxygène de 0,2 - 0,5 MPa, la concentration de la masse de 8-15% du poids, pendant 60 - 120 minutes, dans la température de 110 - 120°C;
- e) blanchiment au chlorite de sodium, au moins deux fois, à la concentration de NaClO₂ de 1 - 1,5% du poids et à la concentration de H₂SO₄ de 0,05 - 0,1% du poids, dans la température de 60 - 70°C, pendant 60 - 120 minutes et extraction alcaline suivante dans la solution de NaOH avec la concentration de 0,5 - 1% du poids, dans la température de 70 - 80°C, pendant 60-120 minutes ;
- f) traitement enzymatique de la masse de la cellulose reçue par la cellulose de l'activité endo-1,4-bêta-glucanase de 10-1000 J/g, par rapport à la masse sec, à la réaction de pH de 4 - 7, dans la température de 40 - 60°C, pendant

- 30-480 minutes, à la vitesse de mélange de 50 - 500 des rotations par la minute, après quoi laver la masse de cellulose à l'eau adoucie et filtrer sous pression réduite et ensuite inactivation de l'enzyme restant dans la masse de cellulose dans la température de 90 - 125°C, pendant 10 - 30 min; 5
- g) homogénéisation de la suspension aqueuse de cellulose à la concentration de 0,5-3% du poids avec la vitesse de rotation de 5000 - 20000 des rotations par la minute pendant 1 - 10 minutes, refroidi pendant homogénéisation de la solution de saumure de la température environ - 15°C, et ensuite centrifugation de la suspension avec la vitesse de rotation de 4000 - 15000 des rotations par la minute pendant 5 - 30 minutes pour obtenir le surnageante contenant les nano - fibres celluloses. 10 15
2. Méthode selon la réservation 1 est **caractérisé par le fait que** la liquide de digestion contient 0,1% du poids d'anthraquinone. 20
3. Méthode selon la réservation 1 est **caractérisé par le fait que** la liquide de digestion contient 3 - 6% du poids de H_2O_2 , 0,1 - 0,3% du poids d'acide éthylènediamine - tétracétique, 0,2 - 0,5% du poids de $MgSO_4$ et 2 - 5% du poids de verre soluble. 25
4. Méthode selon la réservation 1 se **caractérise par le fait que**, la masse cellulose après le blanchiment dans l'étape e) est soumis à la délignification additionnelle par l'acide à la concentration de 1 - 2% du poids de l'acide peracétique et de 0,2 - 0,5% du poids de $MgSO_4$, par rapport à la masse sec, dans la température 80 - 90°C, pendant 60-120 minutes. 30 35
5. Méthode selon la réservation 1 est **caractérisé par le fait que**, la masse cellulose de l'humidité de 50 - 70% après le blanchiment dans l'étape e) est soumis, avant le traitement enzymatique dans l'étape f), au défibrage mécanique pendant 20 - 90 minutes et ensuite à l'homogénéisation dans une suspension aqueuse. 40 45
6. Méthode selon la réservation 1 ou 2 ou 3 se **caractérise par le fait que**, le sédiment formé après l'homogénéisation et centrifugation dans l'étape g) est retourné à l'étape e). 50

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REFERENCES CITED IN THE DESCRIPTION

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