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(71) Applicants: **SOCIETA' COOPERATIVA SOCIALE IL GIARDINONE** [IT/IT]; Via Milano, snc, 20085 Locate di Triulzi (MI) (IT). **COFFEEFROM S.R.L** [IT/IT]; Galleria del Corso n. 1, 20122 Milano (IT).

(72) Inventors: **DE NARDO, Luigi**; c/o POLITECNICO DI MILANO - Campus Mancinelli, Via Mancinelli 7, 20131 Milano (IT). **PASTORI, Nadia**; c/o POLITECNICO DI MILANO - Campus Mancinelli, Via Mancinelli 7, 20131 Milano (IT). **RIVA, Laura**; c/o POLITECNICO DI MILANO - Campus Mancinelli, Via Mancinelli 7, 20131 Milano (IT). **PUNTA, Carlo**; c/o POLITECNICO DI MILANO - Campus Mancinelli, Via Mancinelli 7, 20131 Milano (IT). **GALLO, Laura**; PIAZZA VITTORIA 7 E, 20085 Locate di Triulzi (MI) (IT). **CASARI, Giancarlo**; PIAZZA VITTORIA 7 D, 20085 Locate di Triulzi (MI) (IT).

(74) Agent: **MORABITO, Sara** et al.; CANTALUPPI & PARTNERS S.R.L., P.tta C. Pedrocchi 18, 35122 Padova (IT).

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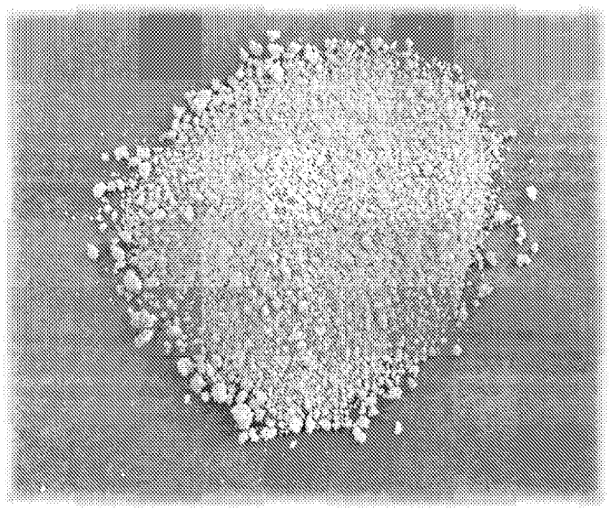

Fig. 1

(57) Abstract: Method for producing oxidized cellulose nanofibres from coffee grounds, comprising the following steps of : dispersing the coffee grounds in an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof, dispersing the processed coffee grounds in an aqueous solution comprising one or more nitroxide radicals and one or more alkali salts or alkali earth salts of HBr, adding an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof, and a base so as to maintain the pH of the dispersion in the range between 10 and 11.5, adding a strong acid until bringing the pH into the range between 1 and 3, filtering, dispersing the filtered oxidized cellulose in a basic aqueous solution at a pH between 7 and 12, defibrating the dispersed oxidized cellulose, adding to the filtered oxidized cellulose dispersion a strong acid until reaching a pH between 1 and 3, obtaining oxidized cellulose nanofibres, filtering.

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METHOD FOR PREPARING OXIDIZED CELLULOSE NANOFIBRES FROM COFFEE GROUNDS AND NANOFIBRES THEREBY OBTAINED

DESCRIPTION

The present invention relates to a method for preparing oxidized cellulose nanofibres from coffee grounds and nanofibres thereby obtained.

Coffee is one of the most popular drinks in the world; what remains following the extraction process of the powder of the roasted coffee beans is an organic waste material, generally called Spent Coffee Grounds (SCG).

Every year, there are generated approximately 20 million tons of SCG which originate from the process of extracting the coffee powder. This by-product is usually managed as waste, both in the domestic sector and in the industrial sector, and finding a possible use for this by-product appears to be of great importance for reducing the impact of the entire chain of coffee on the environment.

There exist a number of studies for the use of such waste in order to generally reduce the quantity thereof and possibly to recycle it so as to limit the simple disposal thereof in dumps, as may happen by using it as a coadjuvant for plant fertilizers or, even better, by recycling it into products which have additional value with respect to the initial value.

In recent years, many studies have focused on the use per se of the depleted coffee, for example, as an absorbent for removing cationic dyes or as a chelator for heavy metals during the treatment of wastewater. However, other studies have targeted the use of the depleted coffee as a prime

material for producing fuel or as a substrate in the cultivation of edible fungi. In recent years, the attention has also been focused on the study of by-products of coffee as sources of bioactive compounds, such as natural phenolic antioxidants, or alkaloids, such as caffeine.

In the prior art, there are known different methods for obtaining nanofibres of oxidized cellulose from organic waste, both of the lignocellulose type and not of this type.

WO2021145291 describes, in the comparative example 2, an oxidation process which is carried out by means of the use of an oxidation catalyst 2,2,6,6-tetramethylpiperidine oxide (commonly known as TEMPO), NaBr, NaClO with food by-products. In this example, coffee grounds are not used but instead okara powder; in addition, the example sets out how it has not been possible to obtain the defibration of the cellulose.

CN112079935 A relates to a method for obtaining nanocellulose from lignocellulose waste which provides for the oxidation by means of a catalytic system which is constituted by TEMPO, NaBr and NaClO. The method provides for this waste to be pre-treated with an acid solution and then with sodium chlorite before the processing with the catalytic oxidation system. In this case, there are also not used any coffee grounds. Therefore, the problem addressed by the present invention is to provide a method for producing such oxidized cellulose nanofibres which is configured to at least partially overcome one or more of the disadvantages set out with reference to the cited prior art.

In the context of this problem, an object of the invention is to provide a process for obtaining oxidized cellulose

nanofibres from coffee grounds which is effective and allows nanofibres to be obtained with a good yield and under bland reaction conditions.

Another object is to provide oxidized cellulose nanofibres which are obtained with this process.

This problem is solved and these objects are achieved by the invention by means of a method for producing oxidized cellulose nanofibres from coffee grounds, comprising one or more of the features mentioned in the appended claims. In particular, there is provided a method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds.

The method for producing oxidized cellulose nanofibres from coffee grounds of the present invention comprises the following steps:

a) dispersing the coffee grounds in an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof, obtaining processed coffee grounds;

b) filtering the processed coffee grounds;

c) dispersing the processed coffee grounds in an aqueous solution comprising one or more nitroxide radicals and one or more alkali salts or alkali earth salts of HBr;

d) adding to the dispersion of the step c) an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof, and a base so as to maintain the pH of the admixture in the range between 10 and 11.5;

e) adding a strong acid until bringing the pH into the range between 1 and 3;

f) filtering, obtaining filtered oxidized cellulose;

g) dispersing the filtered oxidized cellulose in a basic aqueous solution at a pH between 7 and 12;
h) defibrating the dispersed oxidized cellulose;
i) adding to the filtered oxidized cellulose dispersion a strong acid until reaching a pH between 1 and 3, obtaining oxidized cellulose nanofibres;
j) filtering, obtaining filtered oxidized cellulose nanofibres.

This allows the production of oxidized cellulose nanofibres from coffee grounds with good yields and under bland reaction conditions.

The cellulose nanofibres obtained are oxidized in a regionally selective manner.

This method further allows oxidation of the cellulose in a regionally selective manner and at the same time allows removal of the aromatic, lignin and hemicellulose components from the starting cellulose.

These components lessen the characteristics of the cellulose fibres obtained.

In particular, this process allows the production of a regionally selective oxidation, partially converting the alcohol groups in the C6 position of the glucopyranose ring in the respective carboxylic groups.

In particular, by subjecting the coffee grounds obtained following the step a) and b) of the method of the invention to an oxidation reaction (step d)) with a catalyst system

based on nitroxide radicals, it is possible to increase the regional selectivity of the oxidation reaction.

In a second aspect thereof, the present invention relates to oxidized cellulose nanofibres which are obtained using this method. The cellulose nanofibres are regionally selectively oxidized in the C6 position.

Advantageously, the cellulose obtained with the method according to the invention is reduced in terms of nanometric fibres and is suitably functionalized with carboxylic groups. The cellulose obtained with the method according to the invention is reduced in terms of nanometric fibres functionalized with carboxylic groups in the C6 position.

The regionally selective oxidation in the C6 position limits phenomena of depolymerization and/or breaking of the glucopyranose ring, thereby ensuring the structural integrity of the nanofibre obtained with the method of the invention.

This allows a product with greater quality to be obtained.

Furthermore, the regionally selective oxidation allows the method of the invention to provide a cellulose product having predictable and stable characteristics over time.

Therefore, it is obtained a quality control of the cellulose product which otherwise cannot be obtained.

The oxidation reaction of the step a) allows elimination of the aromatic, lignin and hemicellulose components from the starting cellulose. The dispersion of the coffee grounds in an aqueous solution with one or more nitroxide radicals and

one or more alkali salts or alkali earth salts of HB allows a regionally selective oxidation to be subsequently carried out.

In particular, using one or more nitroxide radicals and one or more alkali salts or alkali earth salts of HBr for oxidizing the coffee grounds according to the present invention leads to the partial conversion of the alcohol groups in the C6 position of the glucopyranose ring to the corresponding carboxylic groups.

The oxidation step d) in the presence of the nitroxide radicals and one or more alkali salts or alkali earth salts of HBr allows the production of a partial regionally selective oxidation of the alcohol groups in the C6 position of the glucopyranose ring of the cellulose of the coffee grounds.

Owing to the method of the invention there is obtained a degree of functionalization with carboxylic groups in the C6 position within a range between 0.3 and 1.9 mmol per gramme of product.

The selective oxidation of the hydroxylic group in the C6 position in the carboxylic group further allows a reduction in the energy expenditure of the method of the invention. In fact, the presence of carboxylic groups in the C6 position involves a smaller energy expenditure in the defibration step h) which leads to the production of the single nanofibres. In fact, at a pH greater than 7 there is generated an electrostatic repulsion between the negative charges of the deprotonated carboxylic groups which are introduced into the nanofibres and this facilitates the defibration.

Furthermore, this functionalization improves the compatibility of the cellulose obtained with polar substances, such as, for example, polar polymers, and may be used to obtain additional and subsequent functionalizations of the cellulose itself, as a result of the greater reactivity of the carboxylic group.

With the method of the invention, therefore, there is obtained a product which can more readily be subjected to additional and subsequent selective functionalizations.

Furthermore, this regionally selective oxidation is obtained without any need for subjecting the starting cellulose to pre-processing steps which are usually expensive in terms of energy and time.

The term "nitroxide radical" is intended to be understood to be a stable radical compound of the ammidoxile type having a general formula $R_1R_2N\text{-}O\cdot$, where the substituents R_1 and R_2 are alkyl groups or immidoxile groups, where one or both substituents R_1 and R_2 are carbonylic groups.

The term "strong acid" is intended to be understood to be an acid with an acid dissociation constant (Ka) greater than 1.

Preferred features of the invention are more generally defined by the dependent claims.

In some embodiments, the aqueous solution of the step a) comprises NaClO.

In some preferred embodiments, the aqueous solution of the step a) comprises NaClO, preferably at a percentage concentration between 2% and 15% by weight/volume, more preferably between 3% and 13% by weight/volume, even more preferably between 4% and 8% by weight/volume.

The term "percentage concentration by weight/volume" is intended to be understood to be the grammes of solute dissolved in 100 ml of solution. An aqueous solution of NaClO at 5% by weight/volume therefore contains 5 g of NaClO in 100 ml of solution.

In some embodiments, the step a) for processing the coffee grounds with an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof is carried out for a time between 30 minutes and 4 hours, preferably between 1 hour and 3 hours.

In some embodiments, the ratio between the ml of the aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof and the grammes of the coffee grounds in the step a) is in the range from 5 to 20, preferably from 10 to 15.

This ratio between the aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof and coffee grounds is a good compromise between the need to maintain the dispersion of the step a) in an agitated state and to minimize the volumes involved.

In some embodiments, the step b) of filtering the processed coffee grounds is followed by one or more washes with water, preferably until bringing the pH of the washing solution into

a range between 7 and 8, more preferably between 7 and 7.5, before the step c).

Advantageously, this allows processed coffee grounds which substantially do not have any basic residues to be obtained.

In some embodiments, the steps a) and b) are repeated successively for a number of times between 0 and 6, preferably between 1 and 5, even more preferably between 2 and 4.

In particular, a successive repetition for a number of times equal to 0 is intended to be understood to mean that the steps a) and b) are carried out one single time and in the order in which the step a) precedes the step b); similarly, a successive repetition for a number of times equal to 1 is intended to be understood to mean that the steps a) and b) are repeated successively and give the following sequence: a), b), a), b).

Advantageously, this makes the step of oxidation of the cellulose more efficient, with a simultaneous removal of the aromatic, lignin and hemicellulose components.

Therefore, there is obtained a product which is advantageously pure and substantially does not have any components which are naturally present in the natural cellulose but which can impair the quality of the cellulose nanofibres.

In some embodiments, the one or more nitroxide radicals of the step c) are selected from the group which is constituted

by piperidine nitroxides, pyrrolidine nitroxides and indolinone nitroxides.

A number of examples of these compounds are 2,2,6,6-tetramethylpiperidine oxide (TEMPO) and 2,2,5,5-tetramethylpiperidine oxide.

Preferably, the nitroxide radial of the step c) is a piperidine nitroxide, more preferably 2,2,6,6-tetramethylpiperidine oxide.

In some embodiments, the ratio by weight between processed coffee grounds and the one or more nitroxide radicals in the step c) is in the range from 20 to 60, preferably from 35 to 50.

In some embodiments, the ratio by weight between the one or more nitroxide radicals and the one or more alkali salts or alkali earth salts of HBr in the step c) is in the range from 0.05 to 0.5, preferably from 0.1 to 0.3.

This advantageously allows a greater regional selectivity to be provided in the oxidation process, minimizing phenomena of depolymerization of the cellulose in favour of selective conversion of the alcohol groups in the C6 position of the glucopyranose ring to the corresponding carboxylic groups.

In some preferred embodiments, the aqueous solution of the step d) comprises NaClO, preferably at a percentage concentration between 5% and 20% by weight/volume, more preferably between 5% and 10% by weight/volume.

Preferably, the aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof of the step d) has a molarity between 2 M and 6 M, preferably between 3 M and 5 M.

In some embodiments, the dispersion of the step d) is maintained under agitation, preferably for a time between 6 and 24 hours, more preferably for a time between 12 hours and 2 hours, before the step e).

In some embodiments, the dispersion of the step d) is maintained under agitation at a temperature between 0°C and 30°C, preferably between 15°C and 25°C, before the step e).

In some embodiments, the strong acid which is added in the step e) is selected from the group constituted by hydracids and oxyacids.

By way of non-limiting example, the hydracids include, for example, HCl while the oxyacids include, for example, H_2SO_4.

In some embodiments, the strong acid which is added in the step e) is a halogen hydride acid: in some preferred embodiments, the halogen hydride acid is HCl.

In some embodiments, the strong acid which is added in the step e) has a molarity between 0.1 M and 1 M, preferably between 0.3 M and 0.8 M.

In some embodiments, the step f) of filtration, obtaining filtered oxidized cellulose, is followed by a step f1) for carrying out one or more washes with water, preferably until bringing the pH of the washing solution into a range between 6 and 8, more preferably between 6.5 and 7.5.

This allows the production of filtered oxidized cellulose which substantially does not have any acid residues and which is therefore able to be degraded or to induce degradation if used together with other components.

In some embodiments, the method comprises a step f2) of drying these filtered oxidized cellulose nanofibres following the step f) and preceding the step g).

If the step f1) is also present, the step f2) follows the step f1) and precedes the step g).

In some embodiments, the basic aqueous solution of the step g) has a pH between 10 and 12.

In some embodiments, the basic aqueous solution of the step g) has a percentage concentration by weight between 0.2% and 5%.

In some embodiments, the step h) of defibrating the oxidized cellulose is carried out by means of a homogenizer or a sonicator.

Advantageously, the use of these instruments allows the oxidized cellulose to be defibrated in an effective and rapid manner, reducing the energy costs connected with this step.

Furthermore, the defibration by means of sonication or homogenization is advantageously carried out with a basic pH because at high pH values, preferably at a pH greater than 7, there is deprotonation of the carboxylic groups.

With this deprotonation, the individual cellulose fibres become negatively charged and therefore repel each other; therefore, the defibration is promoted by the electrostatic repulsion of the negative charges present on the fibres with a basic pH.

In some embodiments, the step j) of filtering, obtaining filtered oxidized cellulose nanofibres, is followed by a step j1) of carrying out one or more washings with water, preferably until bringing the pH of the washing solution into a range between 6 and 8, more preferably between 6.5 and 7.5.

This allows the production of oxidized cellulose nanofibres which substantially do not have any acid residues and which are therefore able to be degraded or to induce degradation if used together with other components, for example, together with one or more polymeric materials.

In some embodiments, the method comprises a step j2) of drying these filtered oxidized cellulose nanofibres following the step j).

If the step j1) is also present, the step j2) follows the step j1). It may be noted that some steps of the method described above can be independent of the order of implementation set out. Furthermore, some steps may be optional. Furthermore, some steps of the method can be carried out repetitively or can be carried out in series or in parallel with other steps of the method.

The features and advantages of the invention will be better appreciated from the detailed description of a number of embodiments thereof which are illustrated by way of non-

limiting example with reference to the appended drawings, in which:

- Figure 1 is a photograph relating to the coffee grounds after the processing with an aqueous solution of NaClO at 5% by weight;
- Figure 2 is a photograph relating to the coffee grounds after the processing with 2,2,6,6-tetramethylpiperidine oxide and KBr in an aqueous solution;
- Figure 3 sets out the FTIR-ATR spectrum of the initial coffee grounds after the steps a) and b) and immediately before the step c), after the step e) according to a first embodiment and oxidized cellulose nanofibres obtained from cotton linters;
- Figure 4 sets out a number of micrographs which are obtained by transmission electron microscope of the oxidized cellulose nanofibres according to the invention and
- Figure 5 sets out the FTIR-ATR spectrum of the coffee grounds after the steps a) and b) and immediately before the step c) and after the step e) according to a second embodiment;
- Figure 6A sets out the molecular structure of the natural cellulose, Figure 6B sets out the structure of the cellulose obtained with the method of the invention.

Embodiments

As a result of the invention, there is obtained a cellulose which is partially and regionally selectively oxidized as an evident result of the comparison between Figures 6A and 6B. Figure 6A sets out the molecule of the natural cellulose, which is available in nature. In this molecule, an alcohol group (-OH) is linked to the carbon atoms C2, C3 and C6. By subjecting the cellulose to the method of the invention, there is obtained a cellulose in which the alcohol groups (-

OH) which are linked to the C6 carbon are partially substituted by carboxylic groups (-COOH), as can clearly be seen from the molecule set out in Figure 6B.

The other alcohol groups (-OH) of the C2 and C3 carbon remain present while some of the alcohol groups which are linked to the C6 carbon are substituted by carboxyl groups (-COOH).

Example 1

100 g of damp coffee grounds, corresponding to 40 g of dry coffee grounds, are dispersed in 500 ml of an aqueous solution at 5% by weight of NaClO and left to react for approximately two hours under agitation at ambient temperature. At the end of the two hours, the dispersion is filtered, obtaining a solid residue which is brown in colour.

The dispersion in 500 ml of an aqueous solution at 5% by weight of NaClO and the subsequent filtration are repeated another two times under the same conditions.

At the end of the third filtration, there is obtained a solid product which has a creamy-white colour and which is washed with 500 ml of water and left to dry in air. An image of this product is set out in Figure 1.

There are obtained 20.4 g of dry product, which is called M10, with a weight yield of 51%.

Subsequently, 10 g of this dry product are added to a beaker containing 0.570 l of deionized water, 0.215 g of TEMPO and 1.542 g of KBr.

There are dropped into the dispersion, which is maintained under agitation, 43.7 ml of 12% w/v NaClO and 4 M NaOH in such quantities as to maintain the pH at a value between 10.5 and 11.

The admixture is left under agitation for 18 hours at ambient temperature. At the end, there is added to the beaker a 0.5 M solution of HCl until reaching a pH between 1 and 2.

Finally, the dispersion is filtered over a Buchner filter and washed with deionized water until neutral condition.

There is obtained a solid product in the form of a fine powder which is white/grey in colour and which is left to dry in air. An image of this product is set out in Figure 2.

There are obtained 5 g of dry product which is constituted by oxidized cellulose and which is called TO_M10, with a weight yield of 50%.

Figure 3 sets out the FTIR-ATR spectrums of the coffee grounds (Fondo), the product M10, the product TO_M10 and an oxidized cellulose which is obtained with cotton linters (TOC) under the same reaction conditions used for the coffee grounds.

The FT-IR spectrums in the solid phase of the samples have been obtained by using a Varian 640-IR spectrometer which is provided with an accessory ZnSe ATR. All the samples have been treated with 0.1 N HCl before the acquisition of the spectrums.

Subsequently, a dispersion at 1% w/v of TO_M10 in deionized water is prepared.

This dispersion is obtained by dispersing 500 mg of TO_M10 in 50 ml of deionized water.

Subsequently, there are added 5 drops of 1 M NaOH so as to obtain a pH of approximately 10 and the dispersion is ultrasonicated for 10 minutes by means of a sonicator with immersion in a bath of water and ice. The dispersion becomes semi-transparent.

This dispersion appears visually to be generally similar to the one obtained by ultrasonic processing of oxidized cellulose nanofibres obtained from cotton linters.

Subsequently, two aliquots of 1.5 ml of the dispersion obtained by dispersing 500 mg of TO_M10 in 50 ml of deionized water are deposited on two slides and 5 drops of 0.5 M HCl are added to one of the two aliquots.

The aliquot treated with HCl is aggregated after the addition of the acid, exactly as occurs for a similar dispersion of oxidized cellulose nanofibres obtained from cotton linters, while the non-acidified one remains fluid and well-dispersed.

Furthermore, by leaving the aliquot which is treated with HCl to dry, there is observed the formation of a transparent two-dimensional film.

A diluted dispersion of nanofibres with a basic pH and with ultrasonic treatment has been observed under a transmission electron microscope (TEM). Some images obtained with an

acceleration voltage of 200 kV by means of TEM Philips CM 200 (Koninklijke Philips N.V., Amsterdam, Netherlands) are set out in Figure 4. From the analysis of these micrographs, the nanometric dimension of the cellulose nanofibres obtained with this method becomes evident.

In particular, the nanofibres which are obtained with the method according to the invention have a diameter with a dimension distribution between 5 and 20 nm, mainly between 5 and 15 nm, and a length between 100 and 800 nm, mainly between 200 and 400 nm.

Example 2

25 g of damp coffee grounds corresponding to 10 g of dry coffee grounds are dispersed in 250 ml of a 5% aqueous solution in a reaction flask which is provided with a reflux condenser and the dispersion is heated to 100°C in an oil bath and left under agitation for a time of 8 hours. At the end of the 8 hours, the dispersion is filtered and the solid residue, which is brown in colour, is washed with 250 ml of deionized water and finally left to dry in air.

There are obtained 6 g of dry product which is called M10-hot with a weight yield of 60%.

Example 3

25 g of damp coffee grounds corresponding to 10 g of dry coffee grounds are dispersed in 250 ml of a 12% aqueous solution by weight of NaClO in a bath of water and ice.

The dispersion is left to react under agitation over night after which it is filtered and the solid obtained in this

manner, which is yellowish in colour, is washed with 250 ml of deionized water.

There is obtained 1 g of dry product, which is called M8, with a weight yield of 10%. Subsequently, 1 g of M8 is added to a beaker containing 0.057 l of deionized water, 0.0215 g of TEMPO and 0.1542 g of KBr.

There are dropped into the dispersion, which is maintained under agitation, 4.37 ml of 12% w/v NaClO and 4 M NaOH at such a quantity as to maintain the pH at a value between 10.5 and 11.

The admixture is left under agitation for 18 hours at ambient temperature. At the end, there is added to the beaker a 0.5 M solution of HCl until reaching a pH between 1 and 2.

Finally, the dispersion is filtered over a Buchner filter and washed with deionized water until neutral.

A solid product which is light brown in colour is obtained and left to dry in air.

There are obtained 0.35 g of dry product which is called TO_M8 with a weight yield of 35%.

Figure 5 sets out the FTIR-ATR spectrums of M8 and TO_M8; from the comparison of the two spectrums and in particular the appearance of the absorption band at approximately 1740 cm^{-1}, which can be attributed to the stretching signal of the carbonyl C=O of the carboxylic group COOH, the efficacy of the treatment with TEMPO is evident in terms of selectively oxidizing the coffee grounds before being treated with NaClO.

Example 4

2500 g of damp coffee grounds corresponding to 1000 g of dry coffee grounds are dispersed in 5 l of a 5% aqueous solution by weight of NaClO in an 8 l container and left to react for 1 hour under agitation at ambient temperature by using a bladed agitator. At the end, the admixture is filtered.

The dispersion in 5 l of a 5% aqueous solution by weight of NaClO and the subsequent filtration are repeated another 4 times under the same conditions.

At the end of 5 washes with NaClO, there is obtained a solid product which is creamy white in colour and which is washed with 5 l of water and left to dry in air.

There are obtained 700 g of dry product which is called M10_scale-up, with a weight yield of 70%.

Subsequently, 100 g of M10_scale-up are added to a container which contains 5.7 l of deionized water, 2.15 g of TEMPO and 15.42 g of KBr.

There are dropped in the dispersion, which is maintained under agitation, 437 ml of 12% w/v NaClO and 4 M NaOH at such quantities as to maintain the pH at a value between 10.5 and 11.

The admixture is left under agitation for 18 hours at ambient temperature. At the end, a 0.5 M solution of HCl is added to the beaker until reaching a pH between 1 and 2.

Finally, the dispersion is filtered over a Buchner filter and washed with deionized water until neutral condition.

There is obtained a solid product which is creamy white in colour and which is left to dry in air.

There are obtained 28.5 g of dry product, which is called TO_M10_scale-up, with a weight yield of 30%.

Naturally, in order to comply with specific and contingent application requirements, a person skilled in the art may apply to the above-described solution additional modifications and variants which are still included within the scope of protection as defined by the appended claims.

CLAIMS

1. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds, comprising the following steps:

a) dispersing the coffee grounds in an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof, obtaining processed coffee grounds;

b) filtering the processed coffee grounds;

c) dispersing the processed coffee grounds in an aqueous solution comprising one or more nitroxide radicals and one or more alkali salts or alkali earth salts of HBr;

d) adding to the dispersion of the step c) an aqueous solution comprising one or more of HClO, $HClO_2$ and the salts thereof, and a base so as to maintain the pH of the dispersion in the range between 10 and 11.5;

e) adding a strong acid until bringing the pH into the range between 1 and 3;

f) filtering, obtaining filtered regionally selectively oxidized cellulose;

g) dispersing the filtered regionally selectively oxidized cellulose in a basic aqueous solution at a pH between 7 and 12;

h) defibrating the dispersed regionally selectively oxidized cellulose;

i) adding to the filtered regionally selectively oxidized cellulose dispersion a strong acid until reaching a pH between 1 and 3, obtaining oxidized cellulose nanofibres;

j) filtering, obtaining filtered regionally selectively oxidized cellulose nanofibres.

2. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to claim

1, wherein the step d) is carried out so as to obtain the partial conversion of the alcohol groups (-OH) in the C6 position of the glucopyranose ring in the respective carboxylic groups (-COOH).

3. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to claim 1 or 2, wherein the step d) is carried out so as to obtain a degree of functionalization with carboxylic groups in the C6 position within a range between approximately 0.3 and 1.9 mmol per gramme of product.

4. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of claims 1 to 3, wherein the steps a) and b) are repeated successively for a number of times between 0 and 6.

5. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of claims 1 to 4, wherein the nitroxide radical is 2,2,6,6-tetramethylpiperidine oxide and the ratio by weight between processed coffee grounds and 2,2,6,6-tetramethylpiperidine oxide in the step c) is in the range from 20 to 60.

6. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of the preceding claims, wherein the ratio by weight between the one or more nitroxide salts and the one or more alkali salts or alkali earth salts of HBr in the step c) is in the range from 0.05 to 0.5.

7. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one

of the preceding claims, wherein the aqueous solution of the step a) comprises NaClO, preferably at a percentage concentration between 2% and 15% by weight/volume.

8. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of the preceding claims, wherein the aqueous solution of the step d) comprises NaClO, preferably at a percentage concentration between 5% and 20% by weight/volume.

9. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of the preceding claims, wherein the dispersion of the step d) is maintained under agitation for a time between 6 and 24 hours at a temperature between 0°C and 30°C before the step e).

10. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of the preceding claims, wherein the step h) of defibrating the oxidized cellulose is carried out by means of homogenizers or sonicators.

11. Method for producing regionally selectively oxidized cellulose nanofibres from coffee grounds according to any one of the preceding claims, comprising after the step j) the step j1) of washing the oxidized cellulose nanofibres and/or the step j2) of drying the oxidized cellulose nanofibres, the step j2) where applicable being after the step j1).

12. Regionally selectively oxidized cellulose nanofibres which are obtained using the process according to any one of claims 1 to 11.

13. Regionally selectively oxidized cellulose nanofibres according to claim 12, wherein said cellulose nanofibres have between approximately 0.3 and approximately 1.9 mmol per gramme of product of carboxylic groups which are linked to the C6 carbon of the molecule of cellulose.

Fig. 1

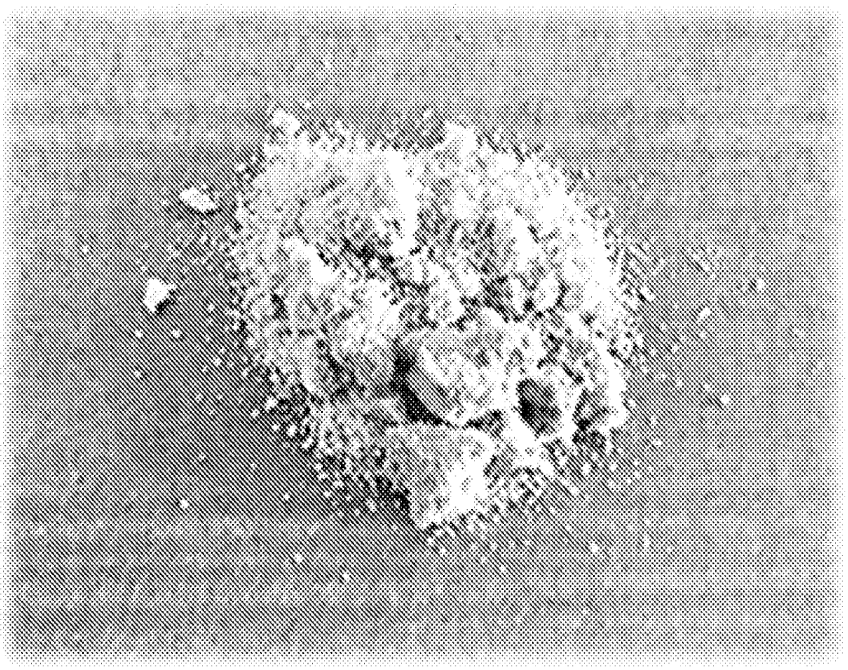


Fig. 2

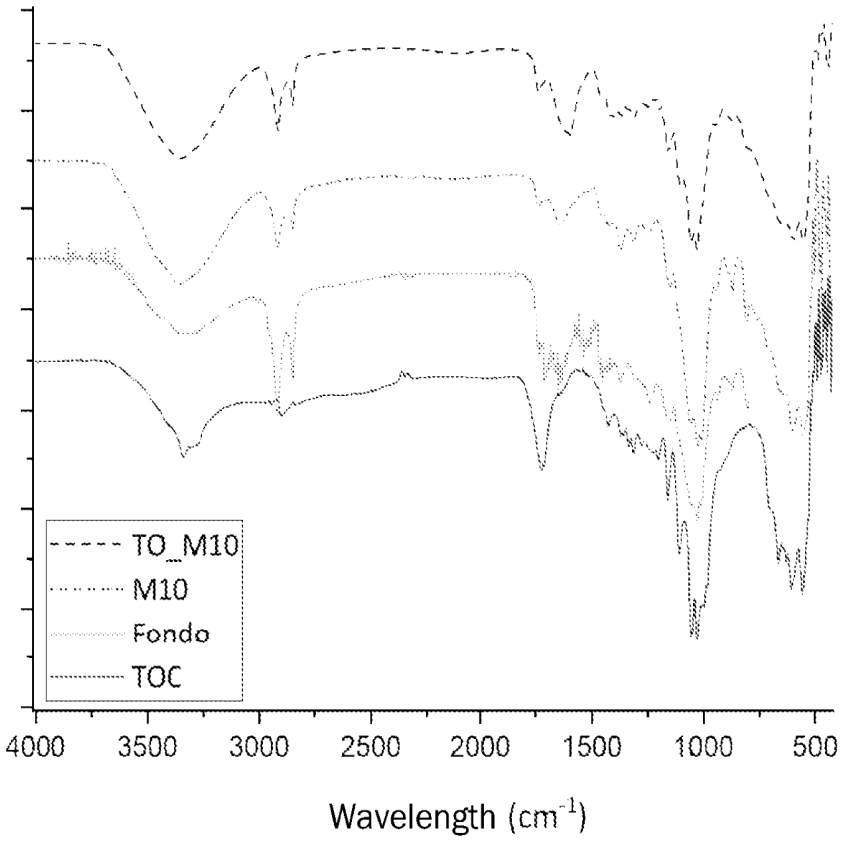

TO_M10
M10
Fondo
TOC
4000
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

Fig. 3

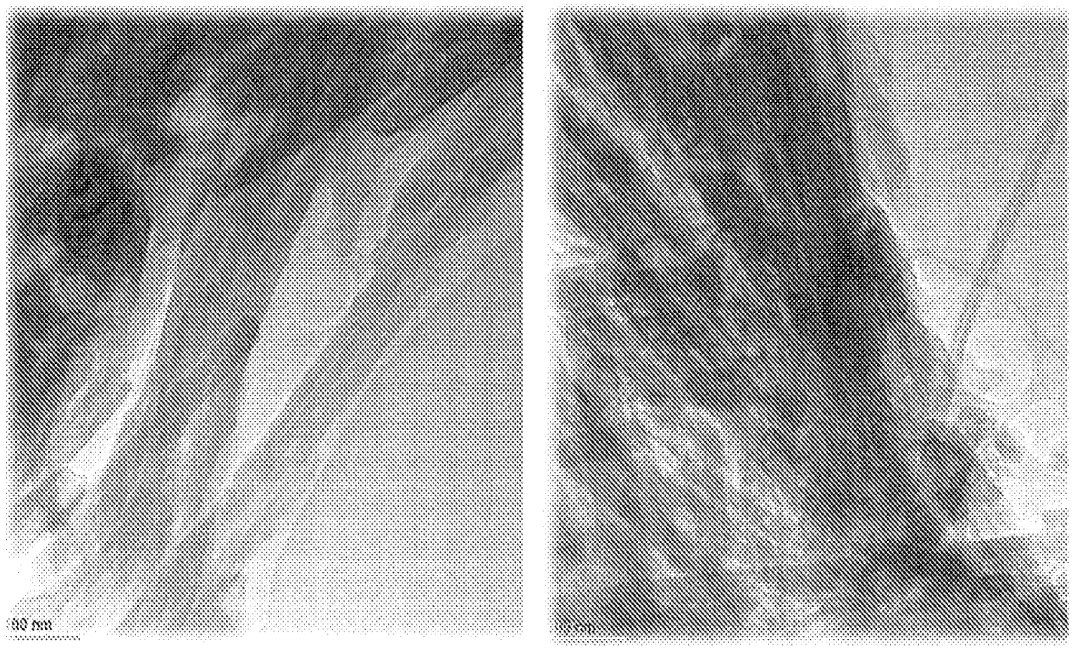
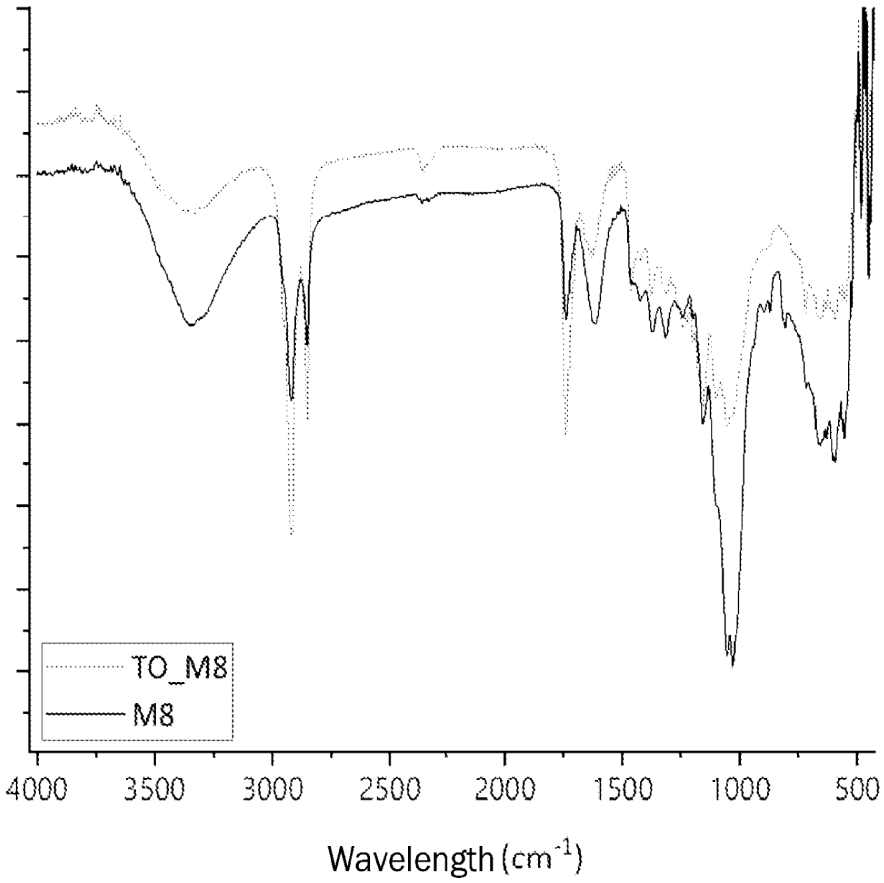

80 nm

Fig. 4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M8
4000
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

Fig. 5

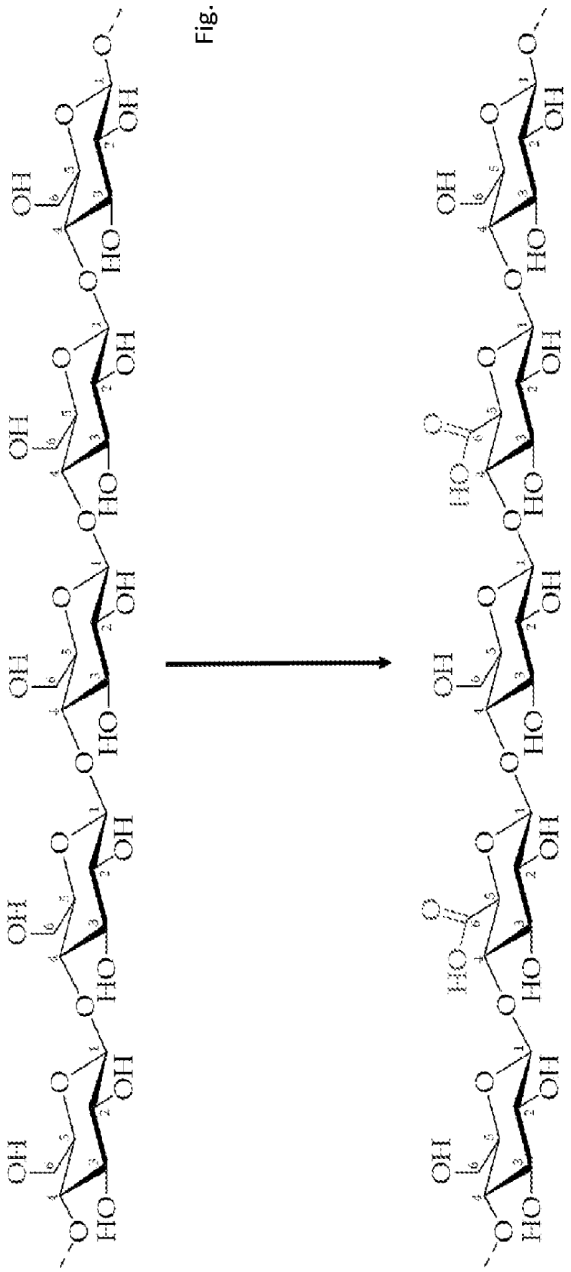

Fig. 6A

Fig. 6B

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2023/055981

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08B15/02 C08L1/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHI CONGCAN ET AL: "Sustainable and superhydrophobic spent coffee ground-derived holocellulose nanofibers foam for continuous oil/water separation", SUSTAINABLE MATERIALS AND TECHNOLOGIES, vol. 28, 1 July 2021 (2021-07-01), page e00277, XP093014167, ISSN: 2214-9937, DOI: 10.1016/j.susmat.2021.e00277 paragraph [2.3.]; figure 1 -----	1-13

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 August 2023	30/08/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Friedrich, Christof