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(54) Title: BIOCHAR-BASED MATERIAL AND METHOD OF ITS PREPARATION

(57) Abstract: Biochar-and-graphene-oxide-based material usable preferably as an absorbent or catalyst, consisting of a composite of biochar and graphene oxide prepared by common oxidation of a mixture of graphite and biochar in the graphite to biochar weight proportions ranging from 1:2 to 3:1, with hydroxyl functional groups bound to its surface. The method of the material preparation consists of the following steps: - mixing biochar and graphite and subjecting the mixture to sulphuric acid and an alkaline metal nitrate, - adding potassium permanganate and the mixture leaving under these oxidation conditions for at least 12 hours, - subjecting the mixture to hydrogen peroxide action in acid environment, - removing sulphate ions from the mixture and adapting its pH to neutral, preferably by washing with water, centrifugation and decanting.



Biochar-based material and method of its preparation

The present invention concerns a biochar-based material for use as absorption material, for example for soil and water remediation or for antimicrobial use. The material can be formed into a foil.

Biochar is a product prepared of waste biomass by dry pyrolysis with limited or no air access at the temperature range of 300 to 600 °C, or by hydrothermal pyrolysis at temperatures around 200 °C.

Biochar is a porous carbonaceous product with a compact hydrophobic core, a prevailing aromatic structure and a shell with hydrophilic properties and properties of an oxygen functional group carrier. Biochar can be used for remediation of soil and water, as absorbent of inorganic and organic pollutants, as a heterogeneous catalyst, as a super capacitor and in many other applications.

The physical and technical properties of biochar are adapted and further improved by modification for various individual applications. The modifications can be performed before, during or after the pyrolysis. The modifications can be chemical, such as oxidation, sulphonation or amidation, changing the surface functional groups by reaction with other monomers or oligomers resulting in development of composite materials. There are also physical modifications including mixing with other components, sonication or turbo grinding.

Liu et al. (RSC Adv. 2016, 6, 24314-24319) prepared nano-composite materials containing biochar and carbonic nano-tubes (biochar-PySA-CNT) or graphene oxide (biochar-PySA-GO) by modification of the biomass by carbonic nano-tubes or graphene oxide with subsequent pyrolysis at 600 °C. This material shows good sorption properties in relation to Pb(II) and Cd(II) in a water suspension, but only exists in particle form.

CN 105055897 A introduces a composite material consisting of graphene oxide modified biochar with the graphene oxide bound to the biochar by means of chitosan. The acid solution of chitosan is mixed with graphene oxide and biochar is added in the

solution. The resulting composite shows excellent sorption ability, especially in relation to Pb(II). However, it does not allow for foil formation.

There is the continuing need to search for and find new materials, especially on the basis of waste product processing, suitable as absorbents for water and soil remediation or as catalysts, with well reproducible structures and in forms permitting their convenient use.

The present invention offers a biochar-and-graphene-oxide-based material usable mainly as an absorbent or catalyst, where a biochar and graphene oxide composite prepared by common oxidation of a graphite and biochar mixture in the weight proportions from 1:2 to 3:1 has hydroxyl functional groups bound to its surface.

This material is the first biochar-and-graphene-oxide-based material which can be formed into a foil. The foil is an easy-to-handle form in comparison to the so far common powder or suspension forms. In a preferred embodiment the foil thickness is at least 6 μm , and in an even more preferable embodiments 7 to 20 μm .

The present invention further provides for a method of preparation of the material in the following steps:

- mixing biochar and graphite and subjecting the mixture to sulphuric acid and an alkaline metal nitrate,
- adding potassium permanganate and the mixture leaving under these oxidation conditions for at least 12 hours,
- subjecting the mixture to hydrogen peroxide action in acid environment,
- removing sulphate ions from the mixture and adapting its pH to neutral, preferably by washing with water, centrifugation and decanting.

The preferred biochar to graphite proportions in the mixture range between 1:2 and 3:1.

In a preferred embodiment the potassium permanganate is added at a temperature below 15°C, and after its addition the mixture is heated to at least 50°C with constant stirring for at least 1 hour.

The material preparation procedure therefore includes mixing biochar with graphite and their common oxidation by the method known to experts in the field as oxidation according to Hummers (Hummers, William S.; Offeman, Richard E. (March 20, 1958). "Preparation of Graphitic Oxide". *Journal of the American Chemical Society* **80** (6): 1339). The use of oxidation according to Hummers, including reactions with sulphuric acid and a nitrate, leads to removal of heavy metals.

A preferred material processing to foil is done by liquid removal from the material in the form of suspension and its drying. The preferred form of the suspension is aqueous suspension. The liquid preferably removed from the suspension by filtration, in the most beneficial way by a Teflon filter. Or alternatively the processing to foil may be performed by centrifugation of the material in the form of suspension with subsequent decanting; the solid state resulting from the decantation then to be evenly spread along a substrate and let dry to form foil. Another option is pouring the suspension and its drying to the foil format.

In a preferred embodiment of the invention the biochar may be exposed to sonication, or treated with H_2O_2 or an organic acid, for example ascorbic acid, before its mixing with graphite. This treatment improves thermal stability of biochar. Sonication in addition removes poly-aromatic substances.

The present invention further includes application of the material that is the subject of the invention as an absorption agent for soil and water remediation, as an additive to soil substrates or as an antimicrobial (disinfecting) material.

The materials according to the present invention, produced by the above-described method, show a unique structure containing free hydroxyl groups on the surface of the oxidation product. In a comparative test of oxidation of biochar alone not mixed with graphite the oxidation product surface did not contain any -OH groups (this was found by infrared spectroscopy measurement). The very presence of the hydroxyl groups allows foil production from the material according to the present invention, assuring formation of a suspension that can be filtrated and possesses surface properties

permitting film formation. On the other hand, the absence of the hydroxyl groups will prevent formation of the suspension that can be filtrated and forms the film.

The drawings demonstrate selected physical properties of the produced biochar.

Fig. 1 shows the FT-IR spectrum of the sample identified as TEST 7.

Fig. 2 shows the FT-IR spectrum of the sample identified as TEST 6.

Fig. 3 shows the FT-IR spectrum of the sample identified as TEST 8.

Fig. 4 shows the FT-IR spectrum of the sample identified as TEST 9.

Material preparation and characterisation:

Mixtures of biochar and graphite was formed with the total weight of 2.25 g in the below proportions of both components. The mixture of biochar and graphite was then mixed with 52 ml of concentrated sulphuric acid and 3 g of NaNO_3 . After cooling of the mixture to 10 °C KMnO_4 was added stepwise in the total quantity of 7 g. After that the reaction mixture was slowly heated to 55 °C, at which temperature the mixtures was stirred intensely for 2 to 3 hours. The resulting product was left to settle at the laboratory temperature for 3 to 4 days. The settled mixture was diluted by distilled water, decanted and mixed with H_2O_2 and HCl . The centrifugation with the decantation was repeated until neutral pH was achieved together with negative reaction to sulphate ions. The centrifuged product was filtered and processed to the film shape by even distribution along a substrate and drying.

The above-described procedure used two types of biochar generated by 17-minute pyrolysis of biomass consisting of 80 wt% of corn silage and 20 wt% of cellulose fibre at 470 °C. We used condensate biochar in most cases, and drift biochar in one case.

The following materials were prepared:

The sample identified as TEST 7 (comparative sample) – with the graphite to biochar proportion of 0:1 (i.e. biochar oxidized in the absence of graphite), condensate biochar.

The sample identified as TEST 6 – with the graphite to biochar proportion of 2:1, condensate biochar.

The sample identified as TEST 8 – with the graphite to biochar proportion of 1:1, condensate biochar.

The sample identified as TEST 9 – with the graphite to biochar proportion of 1:2, condensate biochar.

The sample identified as TEST 10 – with the graphite to biochar proportion of 2:1, drift biochar.

FT-IR spectrums of the prepared samples were measured. The measurements were performed by Bruker Alpha/FT-IR spectrometer, with OPUS 6.5 software, scope 375 to 4000 cm^{-1} .

In the case of the TEST 7 sample no vibrations characterising the –OH groups were identified (see Fig. 1). Weak vibrations of 2670 cm^{-1} , 2604 cm^{-1} can be attributed to C-H, medium-intensity vibrations of 1719 cm^{-1} , 1702 cm^{-1} to carbonyl, and of 1560 cm^{-1} to the aromatic skeleton (C=C bonds), vibrations of 2000 to 2300 cm^{-1} corresponding to the aromatic circle. The strongest absorbance, observed at the maximum of 1074 cm^{-1} , corresponded to the functional groups of C-O, the asymmetric and the symmetric C-O-C, =CO-C or their structural groupings. The absence of the -OH groups was manifested in the course of the product processing by decanting and centrifugation where the thick oily suspension could not be formed (for the reason of absence of the connection by hydrogen bridges), and therefore no film could be produced. The aqueous suspension of this sample was a false solution, dispersed homogeneously and mostly passing through the filter.

In the case of the other samples a band was identified characterising -OH vibrations in the area of 3200 to 3700 cm^{-1} (for the FT-IR spectra see Fig. 2-4). These samples allowed for film formation and foil production. The produced foil thicknesses ranged between 9 and 14 μm .

The prepared samples were also subjected to TG-DTA and TG-DSC analysis: STA i 1500 (Instrument Specialists Incorporated – THASS), air as the degradation medium, air flow rate 20 ml/min., temperature progress 25 to 600°C, speed of sample heating 10°C/min, sample charges TEST 6 2.62 mg, TEST 7 9.64 mg, TEST 8 1.76 mg, TEST 9 1.89 mg, and TEST 10 4.06 mg.

The temperature intervals of the TGA curves defined by intersections of tangents drawn over the respective arches of the TGA curve are shown in the following table:

Sample	Interval No.	Temperature range (°C)	Weight loss (%)
TEST 7	1	12.2 – 40.1	0.6
	2	40.1 – 120.9	11.3
	3	120.9 – 431.7	19.6
	4	437.1 – 599.9	61.9
TEST 6	1	15.1 – 45.3	Rise by 3.9
	2	45.3 – 108.1	12.7
	3	108.1 – 182.9	10.7
	4	182.9 – 230.9	24.7
	5	230.9 – 491.8	22.9
	6	491.8 – 543.5	36.4
TEST 8	1	12.9 – 42.1	0.5
	2	42.1 – 107.3	14.9
	3	107.3 – 183.8	9.9
	4	183.8 – 227.3	29.2
	5	227.3 – 487.3	27.9
	6	487.3 – 520.0	22.4
TEST 9	1	12.2 – 30.8	Rise by 6.6
	2	30.8 – 112.2	14.4
	3	112.2 – 199.9	7.5
	4	199.9 – 243.3	23.0
	5	243.3 – 450.8	20.8
	6	450.8 – 516.2	38.5
	7	516.2 – 533.6	2.1
TEST 10	1	13.6 – 45.2	1.5
	2	45.2 – 116.1	12.8
	3	116.1 – 189.8	7.1
	4	189.8 – 241.4	26.1
	5	241.4 – 462.5	17.2
	6	462.5 – 479.2	+1.6
	7	479.2 – 543.3	36.6

The following table shows the parameters of the ongoing thermal processes (DSC):

Sample	Thermal process	Temperature range (°C)	ΔH (kJ/kg)	Hf1 (mW)	Tmin/max (°C)
TEST 7	1	12.2 – 148.9	712.8	12.2	90.7
	2	375.5 – 599.9	-2418.3	58.6	576.2
TEST 6	1	15.1 – 47.9	286.2	2.9	30.7
	2	177.3 – 263.0	-1005.6	16.9	212.2
	3	458.3 – 591.8	-4001.8	47.7	519.9
TEST 8	1	179.7 – 246.2	-1319.2	20.7	217.1
	2	453.9 – 564.7	-4273.3	44.1	524.2
TEST 9	1	183.3 – 255.9	-1033.3	17.7	230.2
	2	423.2 – 546.8	-3640.7	26.3	488.2
TEST 10	1	13.6 – 178.1	1953.1	9.1	72.5
	2	192.3 – 254.6	-865.5	29.2	226.7
	3	450.9 – 559.5	-3762.2	53.6	530.3

ΔH = thermal colouring of process pursuant to DSC curves, ($\Delta H > 0$ endothermic process, $\Delta H \leq 0$ exothermic process); Hf1 = thermal process peak height on DSC curve in absolute value related to the point corresponding to the thermal process beginning.

Antimicrobial effects of the above-described materials were investigated:

The quantity of 900 μ l of Escherichia coli cloud (E. coli Esco 3954 CNCTC), approximate value 10^8 , in distilled water, was mixed with 100 μ l of the biochar-and-graphene-oxide-based material sample suspension prepared in the above-described way. The quantity of 1 ml of pure bacterial suspension was used as a control sample. The samples were placed in a shaker for 1hr, 6hrs and 24hrs at laboratory temperature. The quantity of 100 μ l was sampled from the thus prepared specimen to a Petri bowl for specification of colonies per 1 ml.

The results are shown in the following table:

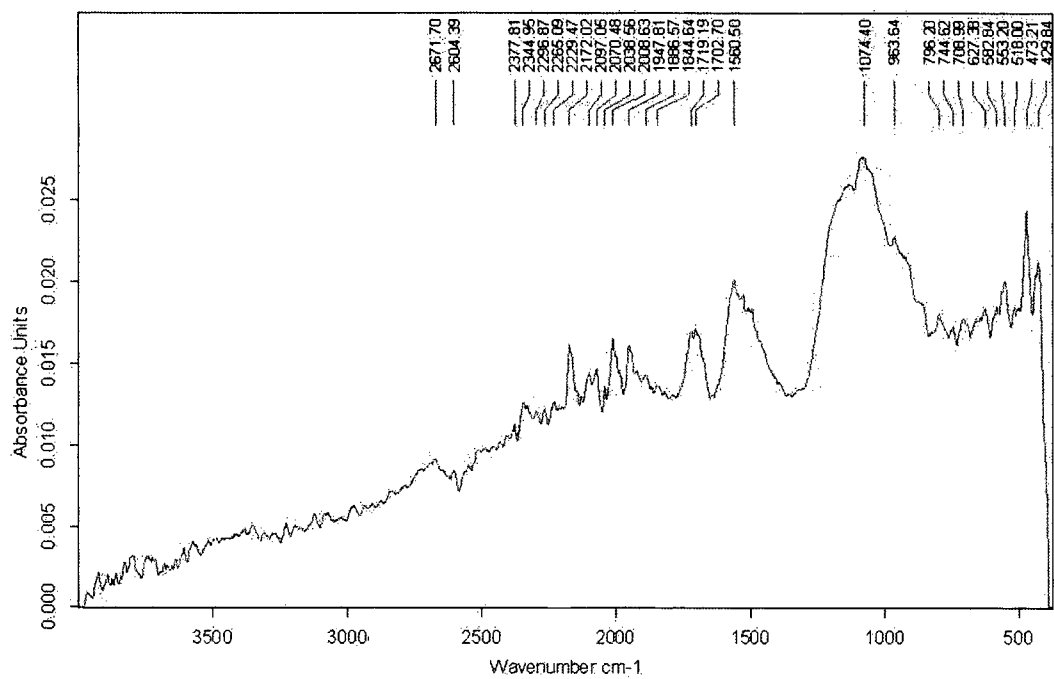
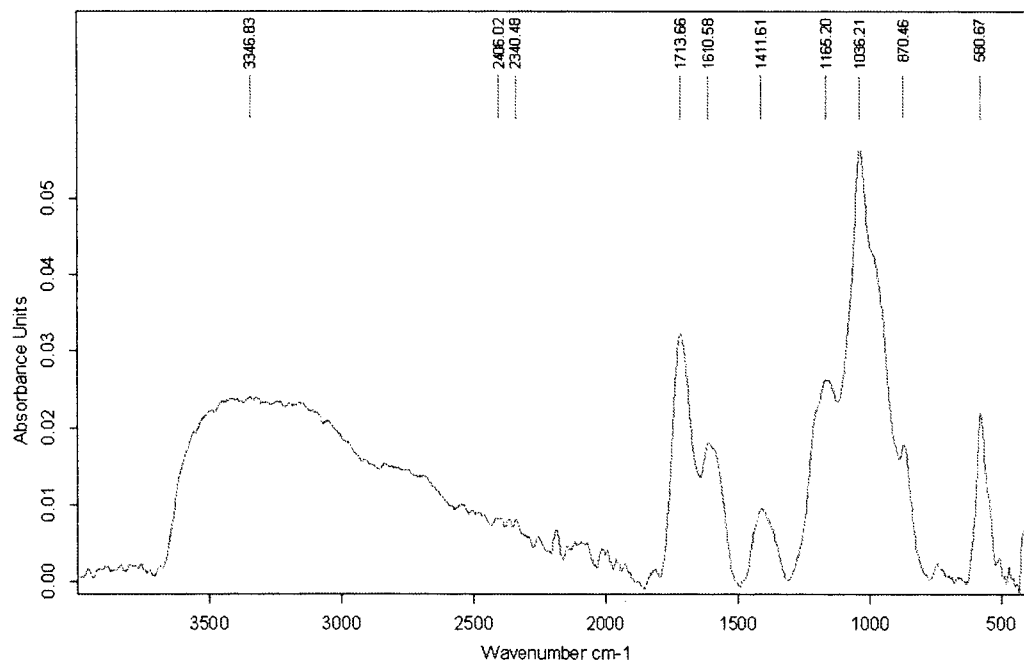
Number of E. coli bacteria in 1 ml				
Time	control	TEST 6	TEST 8	TEST 9
1 hr	$1.2 \cdot 10^8$	$2 \cdot 10^7$	$3 \cdot 10^7$	$6 \cdot 10^7$
6 hrs	$1.2 \cdot 10^8$	$1,5 \cdot 10^6$	$1,8 \cdot 10^6$	$6 \cdot 10^7$
24 hrs	$0.9 \cdot 10^8$	$4 \cdot 10^5$	$4.5 \cdot 10^5$	$4 \cdot 10^7$

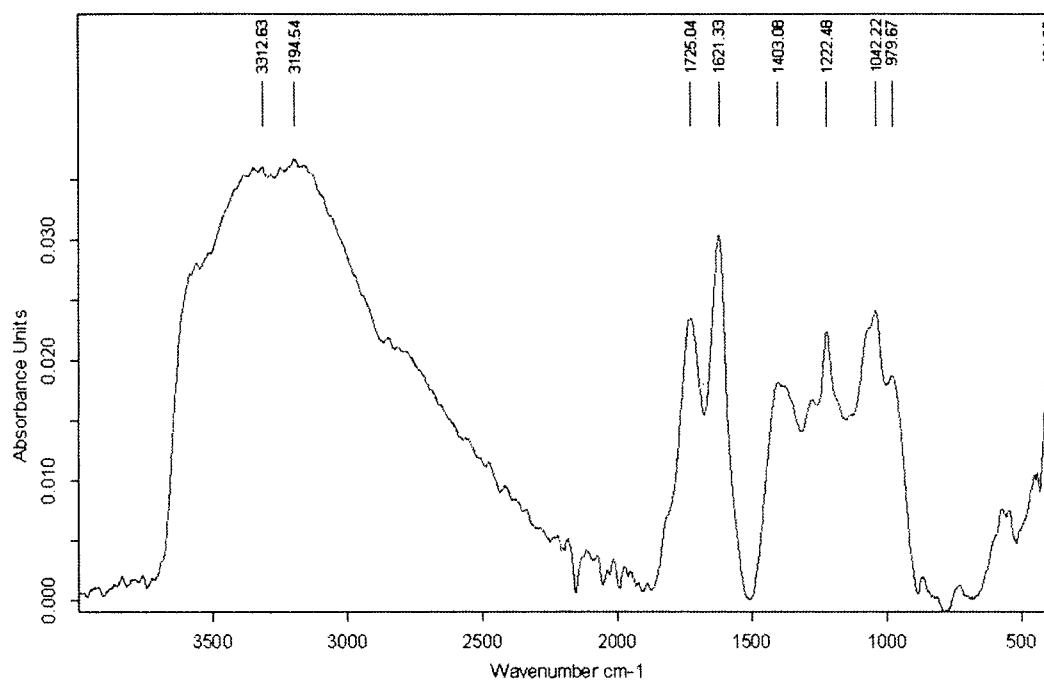
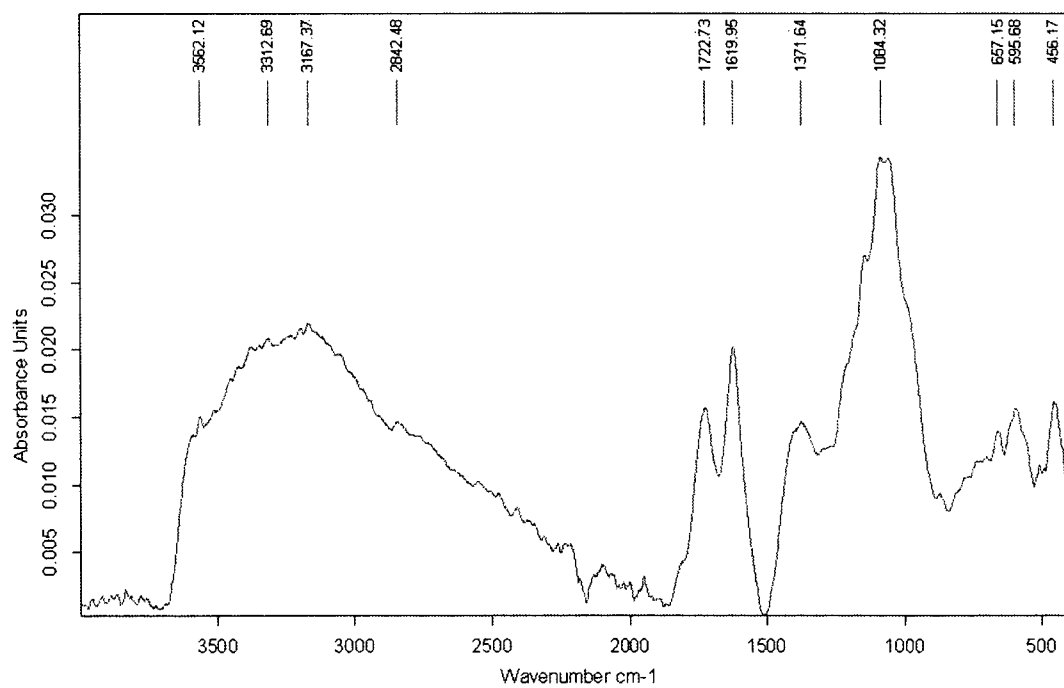
Claims

1. Biochar-and-graphene-oxide-based material applicable as absorbent or catalyst, **characterized in that** a composite of biochar and graphene oxide prepared by common oxidation of a graphite and biochar mixture with the weight proportions of graphite to biochar 1:2 to 3:1 has hydroxyl functional groups bound on its surface.
2. The material according to claim 1, **characterised in that** it is processed to foil with the advantageous thickness of at least 6 micrometers.
3. The method of preparation of the material according to claim 1, **characterised in that** the process includes the following steps:
 - mixing biochar and graphite and subjecting the mixture to sulphuric acid and an alkaline metal nitrate,
 - adding potassium permanganate and the mixture leaving under these oxidation conditions for at least 12 hours,
 - subjecting the mixture to hydrogen peroxide action in acid environment,
 - removing sulphate ions from the mixture and adapting its pH to neutral, preferably by washing with water, centrifugation and decanting.
4. The method according to claim 3, **characterised in that** graphite and biochar are mixed in the biochar/graphite weight proportions of 1:2 to 3:1.
5. The method according to claim 3, **characterised in that** potassium permanganate is added at a temperature below 15°C and the mixture is subsequently heated under constant stirring to at least 50°C for at least 1 hour.
6. The method according to claim 3, **characterised in that** the material is processed to foil by liquid removal from the material in the form of suspension, preferably by filtration through a poly-tetra-fluorine-ethylene filter, and drying in the shape of foil.
7. The method according to claim 3, **characterised in that** the produced mixture is processed to foil by centrifugation and decanting of the material in the form of

suspension and subsequent spreading the material in solid state on a substrate and its drying to foil.

8. The method according to claim 3, **characterised in that** biochar is subjected to sonication, or treatment with H_2O_2 or an organic acid, preferably by ascorbic acid, before its mixing with graphite.
9. Application of the material according to claim 1 as absorption material for soil and water remediation, as an additive to soil substrates or as antimicrobial material.

**Fig. 1****Fig. 2**

**Fig. 3****Fig. 4**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/001286

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B32/198 C01B32/30 B01J20/28 B01J20/20 B01J20/30
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)
C01B B01J

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Lucie Gembalová ET AL: "Biochar-ecological Product and its Application in Environmental Protection", 3 February 2016 (2016-02-03), pages 24-31, XP055446221, Ostrava, Czech Republic Retrieved from the Internet: URL: http://biouhel.cz/wp-content/uploads/2016/03/Biochar1-SUJB.pdf [retrieved on 2018-01-30] abstract page 25, right-hand column ----- -/-	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/001286

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KLOUDA KAREL ET AL: "International Journal of Emerging Technology and Advanced Engineering Joint Oxidation of Fullerene C 60 and Graphite", INTERNATIONAL JOURNAL OF EMERGING TECHNOLOGY AND ADVANCED ENGINEERING, vol. 4, no. 10, 1 October 2014 (2014-10-01), pages 504-522, XP055445808, ISSN: 2250-2459 abstract 2.2.Methodology; page 505, right-hand column table 1 Fig. b; page 507, right-hand column page 508; figure 5 page 520, left-hand column -----	1-9
Y	DATABASE WPI Week 201602 Thomson Scientific, London, GB; AN 2015-75172A XP002777773, -& CN 105 056 897 A (UNIV HUNAN) 18 November 2015 (2015-11-18) abstract claims 1-9 -----	1-9
X,P	GEMBALOVÁ LUCIE ET AL: "Biochar - Ecological Product and Its Application in Environmental Protection", ASIA-PACIFIC ENGINEERING AND TECHNOLOGY CONFERENCE, 25 May 2017 (2017-05-25), pages 22-31, XP055445864, g); page 24 Biochar modification after Pyrolysis e),f); page 24 page 27 Conclusion and Discussion; page 30 -----	1-9
X,P	ROUPCOVÁ PETRA ET AL: "Basic Phytotoxicity of Carbon Foils Prepared by Oxidization of Graphite Combined with Fullerene, Fluorine Graphite and Biochar", ASIA-PACIFIC ENGINEERING AND TECHNOLOGY CONFERENCE, 25 May 2017 (2017-05-25), XP055445804, Experimental Part; page 2 page 4; figures 2a) -2d) -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2017/001286

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 105056897	A	18-11-2015	NONE
