

ACTIVATED CARBON, HYDROCHAR AND PROCESSES FOR MAKING SAME

Field of the Invention

The present invention relates to carbonaceous materials and more particularly to activated carbon, hydrochar and processes for making the same.

5 Background of the Invention

With growing environmental concerns, much attention has been channelled towards the use of sustainable and renewable resources such as biomass. Research has shown that carbonaceous materials such as activated carbon and hydrochar derived from biomass have wide application limited however by
10 properties of the carbonaceous materials. It is therefore desirable to provide carbonaceous materials with improved properties and processes for making the same.

Summary of the Invention

Accordingly, in a first aspect, the present invention provides a process for
15 making activated carbon. The process includes providing a biomass and mixing the biomass with an oxidizing agent to form a biomass-oxidizing agent mixture. The biomass-oxidizing agent mixture is subjected to a hydrothermal carbonization process to form a hydrochar having an increased oxygenated functional group content compared to that of the biomass. The hydrochar is mixed with an activating
20 agent to form a hydrochar-activating agent mixture. The hydrochar-activating agent mixture is subjected to a chemical activation process to form an activated carbon.

In a second aspect, the present invention provides an activated carbon having a mesopore surface area of between about 1300 square metres per gram (m^2/g) and about 2000 m^2/g , a mesopore volume of between about 1.9 cubic
25 centimetres per gram (cm^3/g) and about 3.8 cm^3/g , and a mesoporosity of greater than 70 (%).

In a third aspect, the present invention provides a process for making hydrochar. The process includes providing a biomass and mixing the biomass with an oxidizing agent to form a biomass-oxidizing agent mixture. The biomass-oxidizing agent mixture is subjected to a hydrothermal carbonization process to form
5 a hydrochar having an increased oxygenated functional group content compared to that of the biomass.

In a fourth aspect, the present invention provides a hydrochar having an increased oxygenated functional group content compared to that of a biomass from which the hydrochar is prepared.

10 Other aspects and advantages of the invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, illustrating by way of example the principles of the invention.

Brief Description of the Drawings

Embodiments of the invention will now be described, by way of example only,
15 with reference to the accompanying drawings, in which:

FIG. 1 is a schematic flow diagram illustrating a process for making hydrochar and activated carbon in accordance with one embodiment of the present invention;

FIG. 2 is a photograph showing a biomass of coconut shell;

20 FIG. 3 is a photograph showing a hydrochar prepared from the biomass of coconut shell in accordance with one embodiment of the present invention;

FIG. 4 is a photograph showing the hydrochar of FIG. 3 mixed with an activating agent;

FIG. 5 is a schematic diagram showing a set-up for a chemical activation
25 process in accordance with one embodiment of the present invention;

FIG. 6 is a graph showing nitrogen adsorption-desorption isotherms at 77 Kelvin (K) of a commercially available mesoporous carbon and activated carbons prepared from a biomass of coconut shell with and without pre-chemical activation processing;

5 FIG. 7 is a graph showing pore size distribution of a commercially available mesoporous carbon and activated carbons prepared from a biomass of coconut shell with and without pre-chemical activation processing;

FIG. 8 is a graph showing pore size distribution of activated carbons prepared from a biomass of sawdust with and without pre-chemical activation
10 processing;

FIG. 9 is a graph showing pore size distribution of activated carbons prepared from a biomass of palm kernel shell with and without pre-chemical activation processing; and

FIG. 10 is a graph showing Rhodamine B adsorption curves of a
15 commercially available mesoporous carbon and activated carbons prepared from a biomass of coconut shell with and without pre-chemical activation processing.

Detailed Description of Exemplary Embodiments

The detailed description set forth below in connection with the appended drawings is intended as a description of presently preferred embodiments of the
20 invention, and is not intended to represent the only forms in which the present invention may be practiced. It is to be understood that the same or equivalent functions may be accomplished by different embodiments that are intended to be encompassed within the scope of the invention.

Referring now to FIG. 1, a process 10 for making hydrochar and activated
25 carbon will now be described. The process 10 begins at step 12 by providing a biomass.

The biomass may comprise horticultural waste. In the present embodiment, the biomass may be one or more of coconut shell, palm kernel shell, sawdust, wood, nut shell, husk, fruit pit, seed, peel, bagasse, peat, lignite and sub-bituminous coal and may be provided in the form of coarse granules having a particle diameter
5 of between about 0.5 millimetres (mm) and about 5 mm. In one embodiment, a biomass with high hardness may be selected for improved yield.

At step 14, the biomass is mixed with an oxidizing agent to form a biomass-oxidizing agent mixture.

The oxidizing agent may be one or more of hydrogen peroxide, a carboxylic
10 acid, a peroxy acid, a dibasic acid and a humic acid.

The biomass-oxidizing agent mixture may include between about 60 percent by mass (wt%) and about 80 wt% of the biomass.

The biomass-oxidizing agent mixture is subjected at step 16 to a hydrothermal carbonization process to form a hydrochar (char obtained following
15 hydrothermal treatment) having an increased oxygenated functional group content compared to that of the biomass from which the hydrochar is prepared. Incorporation of the oxidizing agent during hydrothermal treatment of the biomass induces formation of oxygenated functional groups (OFGs) on the hydrochar.

The hydrothermal carbonization process may be performed at a temperature
20 of between about 200 degrees Celsius (°C) and about 300 °C for a period of between about 20 minutes (min) and about 200 min. Hydrothermal carbonization of the biomass is used to improve the chemical characteristics of the hydrochar product (i.e., high concentration of oxygen functional groups and low degree of aromatization) which makes the hydrochar an efficient precursor for subsequent
25 chemical activation.

The hydrochar that is formed may have between about 30 percent (%) and about 70 % more oxygenated functional group content than the biomass. In one

embodiment, the hydrochar has between about 40 % and about 60 % more oxygenated functional group content than the biomass. The hydrochar may have an oxygenated functional group content of between about 1.2 milliequivalent per gram (meq/g) and about 1.6 meq/g. In specific embodiments, the oxygenated functional group content may be about 1.29 meq/g, about 1.42 meq/g or about 1.58 meq/g. The oxygenated functional group content may include one or more of a carboxylic group, a lactonic group and a phenolic group.

At step 18, the hydrochar is mixed with an activating agent to form a hydrochar-activating agent mixture.

The activating agent may be one or more of zinc chloride, phosphoric acid, a metal chloride, an inorganic acid, sodium phosphate and a base. A ratio of the activating agent to the hydrochar in the hydrochar-activating agent mixture may be between about 2:1 and about 10:1.

The hydrochar-activating agent mixture is subjected at step 20 to a chemical activation process to form an activated carbon.

The chemical activation process may be performed at a processing temperature of between about 350 °C and about 650 °C for a period of between about 0.5 hours (h) and about 3 h. The chemical activation process may be ramped to the processing temperature at a rate of between about 5 degrees Celsius per minute (°C/min) and about 15 °C/min. In one embodiment, the chemical activation process may be performed in a presence of nitrogen gas at a flow rate of between about 20 millilitres per minute (ml/min) and about 100 ml/min.

The activated carbon that is formed may have a mesopore surface area of between about 1300 square metres per gram (m^2/g) and about 2000 m^2/g , a mesopore volume of between about 1.9 cubic centimetres per gram (cm^3/g) and about 3.8 cm^3/g , and a mesoporosity of greater than 70 (%), where the mesoporosity is a ratio of the mesopore surface area (A_{me}) to the Brunauer–Emmett–Teller (BET) surface area (A_{t}) of the activated carbon. In one embodiment,

the mesopore surface area may be about 1331 m²/g, the mesopore volume may be about 1.98 cm³/g, and the mesoporosity may be about 76 %. In another embodiment, the mesopore surface area may be about 1780 m²/g, the mesopore volume may be about 3.5 cm³/g, and the mesoporosity may be about 100 %. In yet
5 another embodiment, the mesopore surface area may be about 1815 m²/g, the mesopore volume may be about 2.8 cm³/g, and the mesoporosity may be about 98 %.

With this process 10, activated carbons with high or increased mesoporosity and high or increased mesopore surface area may be obtained from waste biomass.
10 Enhancement of the porosity of the activated carbons is highly desirable and is obtained in the process 10 by choice of the biomass, choice of the oxidizing agent, choice of the chemical activating agent, optimization of activation conditions such as temperature, ramp rate and gas flow rate, and choice of pre-treatment methods.

In the process 10, hydrothermal treatment of the biomass in the presence of
15 an oxidizing agent serves as a pre-treatment step to produce hydrochar with high or an increased OFG content as a precursor for subsequent chemical activation. The pre-treatment step induces the formation of more oxygenated functional groups on the hydrochar, making the hydrochar precursor more reactive during subsequent chemical activation. Chemical activation of the hydrochar with the high or increased
20 OFG content thus produces activated carbons with high or increased mesoporosity and high or increased mesopore surface area.

High mesoporous carbons find application in the field of immobilization of biomolecules such as enzymes, vitamins, etc. High mesoporosity is also highly desirable for energy storage applications, electro-catalysis, electrode materials and
25 environmental remediation applications.

Example

Coconut shells (*cocos nucifera*), palm kernel shells and sawdust were used as waste biomass sources. The coconut shells (after trimming the fibers), the palm

kernel shells (after removing the pulp) and the sawdust were dried at 105°C for 24 hours, crushed using a commercial laboratory blender (Waring) and then ground and sieved to produce coarse granules of about 10 to 20 mesh. A photograph of a biomass of coconut shell is shown in FIG. 2.

5 The biomass is then mixed with an oxidizing agent to form a biomass-oxidizing agent mixture. Hydrogen peroxide (30% GR, Merck) was employed as the oxidizing agent to induce the formation of OFG on the char during pre-treatment of the raw biomass. The pre-treatment with hydrogen peroxide bestows the hydrochar precursor with more OFG content and thus renders it more reactive for subsequent
10 chemical activation.

 The biomass-hydrogen peroxide mixture (15 g biomass in 90 mL H₂O₂ (10% by weight)) was subjected to hydrothermal treatment in a Parr 4848 autoclave at 200°C for 20 min. The reactor was then cooled to room temperature and the products were dried at 105°C for 12 h. A photograph of a hydrochar prepared from
15 the biomass of coconut shell is shown in FIG. 3.

 The activated carbons were subsequently prepared by chemical activation using zinc chloride (ZnCl₂, reagent grade (Scharlab)).

 More particularly, the hydrochar precursor was mixed with a zinc chloride solution (90 mL water in precursor equivalent to 15 g raw biomass) with a zinc
20 chloride to shell ratio of 5:1 and dried at 105°C for 12 h. A photograph showing the hydrochar mixed with an activating agent is shown in FIG. 4. The effect of adding zinc chloride as a chemical activating agent is manifested in the form of two competing mechanisms: micropore formation and pore widening. At low zinc chloride-to-raw material ratios, micropore formation is the dominating effect. Pore
25 widening takes place at the expense of micropore formation for high zinc chloride-to-raw material ratios, thereby reducing the micropore content. Additionally, the amount of the activating agent used depends on the raw material, the presence of

surface functional groups, process conditions, as well as the desired characteristics of the product, for example, pore size, surface area, hardness, etc.

Referring now to FIG. 5, a schematic of a set-up 50 for a chemical activation process is shown. The set-up 50 includes a nitrogen gas source 52 in fluid communication with a furnace 54 (Carbolite). A flow meter 56 is provided to monitor a gas flow from the nitrogen gas source 52 to the furnace 54. An outlet of the furnace 54 is in fluid communication with a scrubber 58.

The hydrochar-activating agent mixture 60 was loaded onto an alumina boat inside a quartz tube and then placed in the furnace 54. The temperature in the furnace 54 was ramped to 500°C at a rate of 10 °C/ min in the presence of nitrogen gas at a flow rate of 50 mL/min and held for 2 hours. The temperature in the furnace 54 was subsequently cooled to room temperature in the presence of nitrogen gas at a flow rate of 50 mL/min. The resultant product was stirred for 30 min in 250 mL of hydrochloric acid (37%, Panreac) (about 0.1 mol/L) and washed with abundant distilled water until a pH of 6 was obtained from the rinse. Finally, the activated carbon was dried at 105°C for 24 h and used for analysis.

Sodium hydroxide (Merck, EMSURE, >99%) was used to measure the OFG content. Boehm titration was carried out for estimation of the oxygenated functional groups which are typically carboxylic, lactonic and phenolic. More particularly, the biomass and hydrochars were heated up to 150°C for 24 h in the presence of a nitrogen (N₂) inert atmosphere. After cooling to room temperature, 1.5 g of the sample was mixed with 50 mL NaOH (0.05M) and the mixture was agitated by shaking for 24 h. The sample was then removed by filtration and 10 mL aliquots were titrated with 0.05M HCl to obtain the OFG content.

Adsorption-desorption isotherms, Brunauer–Emmett–Teller (BET) surface area (A_t) and pore volume of the adsorbents were obtained by using a gas sorption analyzer (Nova-3000 Series, Quantachrome). The NLDFT (Nonlocal Density Functional Theory) method was used for obtaining pore size distribution. In

addition, the mesoporous surface area (A_{me}) and micropore volume was determined using the t-plot method in which the total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.98. The mesoporous volume (V_{me}) was then calculated by subtracting the micropore volume (V_{mi}) from the total pore volume (V_t). Rhodamine B was chosen as a model adsorbate to evaluate the adsorption capacity of the activated carbons. Adsorption experiments were carried out using batch equilibration and the concentrations of the dye were estimated by using a UV-Visible spectrometer (Shimadzu-3600).

Table 1 below shows the OFG content of the biomass before and after the hydrothermal carbonization process.

Table 1

Sample	OFG content (meq/g)
Coconut Shell (CS)	1.04
CS hydrochar	1.58
Saw dust (SD)	0.95
SD hydrochar	1.42
Palm Kernel Shell (PKS)	0.89
PKS hydrochar	1.29

As can be seen from Table 1 above, the hydrochar that is formed has an increased oxygenated functional group content compared to that of the biomass from which the hydrochar is prepared. From the experimental data, it can also be seen that the hydrochar that is formed as a result of the pre-treatment step has between about 40 % and about 60 % more oxygenated functional group content than the biomass from which the hydrochar is prepared.

Table 2 below shows the characteristics of various carbon samples: commercial mesoporous carbon (Sigma Aldrich), activated carbon prepared by direct chemical activation of raw coconut shell (CS-ZP), activated carbon prepared from raw coconut shell that underwent hydrothermal pre-treatment in the presence

of hydrogen peroxide (CS-HHTZP), activated carbon prepared by direct chemical activation of palm kernel shell (PKS-ZP), activated carbon prepared from palm kernel shell that underwent hydrothermal pre-treatment in the presence of hydrogen peroxide (PKS-HHTZP), activated carbon prepared by direct chemical activation of
 5 sawdust (SD-ZP), and activated carbon prepared from sawdust that underwent hydrothermal pre-treatment in the presence of hydrogen peroxide (SD-HHTZP).

Table 2

Sample	BET surface area (A_t , m ² /g)	Mesopore surface area (A_{me} , m ² /g)	Total pore volume (V_t , cm ³ /g)	Mesopore volume (V_{me} , cm ³ /g)	Meso- porosity (A_{me}/A_t)
Commercial mesoporous carbon	201	201	0.48	0.48	100
CS-ZP	1843	1305	2.31	1.99	71
CS-HHTZP	1850	1815	2.87	2.80	98
PKS-ZP	1215	676	1.34	1.07	56
PKS-HHTZP	1742	1331	2.21	1.98	76
SD-ZP	1829	1478	2.28	2.02	80
SD-HHTZP	1780	1780	3.5	3.5	100

As can be seen from Table 2 above, the activated carbons obtained by hydrothermal treatment with hydrogen peroxide and chemical activation using zinc
 10 chloride have high mesopore area, mesopore volume and mesoporosity. It can also be seen from Table 2 above that a significant increase in these attributes is observed when the biomass is pre-treated with hydrogen peroxide in a hydrothermal environment. In fact, it can be seen from Table 2 above that the use of hydrogen peroxide in the hydrothermal step resulted in activated carbon with high
 15 mesoporosity (mesopore area/BET area) of up to 100%, high mesopore surface area of up to 1815 m²/g, and high mesopore volume of up to 3.5 cm³/g. The results substantiate the inference that the inclusion of the oxidizing agent pre-treatment process improves the effectiveness of the activating agent and resulted in a higher

mesopore area and a higher mesoporosity. The high OFG content on the hydrochar followed by zinc chloride activation facilitates formation of significantly high mesoporosity compared to carbons prepared in the absence of hydrogen peroxide pre-treatment. The significant enhancement in both mesopore surface area and
5 volume is attributed to the improved chemical activation resulting from increased OFG formation on the hydrochar through surface functionalization induced by hydrogen peroxide.

Referring now to FIG. 6, a graph of nitrogen adsorption-desorption isotherms of a commercially available mesoporous carbon and activated carbons prepared
10 from a biomass of coconut shell with and without pre-chemical activation processing at 77 Kelvin (K) is shown. The continuous lines represent adsorption and symbols represent desorption. Hysteresis confirms the presence of mesopores. It is evident from FIG. 6 that the volume adsorbed is higher for activated carbon prepared from biomass that underwent hydrothermal pre-treatment in the presence of hydrogen
15 peroxide (CS-HHTZP) compared to activated carbon prepared by direct chemical activation of biomass (CS-ZP) and commercial mesoporous carbon. This demonstrates the importance of hydrothermal pre-treatment of the biomass in the presence of an oxidizing agent prior to chemical activation.

Referring now to FIGS. 7, 8 and 9, a graph of pore size distribution of a
20 commercially available mesoporous carbon and activated carbons prepared from a biomass of coconut shell with and without pre-chemical activation processing is shown in FIG. 7, a graph of pore size distribution of activated carbons prepared from a biomass of sawdust with and without pre-chemical activation processing is shown in FIG. 8, and a graph of pore size distribution of activated carbons prepared from a
25 biomass of palm kernel shell with and without pre-chemical activation processing is shown in FIG. 9. These results demonstrate that the activated carbons prepared with hydrothermal pre-treatment in the presence of the oxidising agent provide better mesoporosity and greater mesopore volume in the range of 50 angstrom (Å) to 100 Å when compared with the activated carbons prepared by direct chemical
30 activation of the biomasses.

Referring now to FIG. 10, a graph of rhodamine B adsorption curves of a commercially available mesoporous carbon and activated carbons prepared from a biomass of coconut shell with and without pre-chemical activation processing is shown. The graph shows the amount of dye adsorbed per gram of activated carbon (5 q_e) at different equilibrium concentrations of the adsorbate in the liquid phase (C_e). The results of the batch equilibrium studies shown in FIG. 10 confirm the higher adsorption capacity of activated carbon prepared from biomass that underwent hydrothermal pre-treatment in the presence of hydrogen peroxide (CS-HHTZP) compared to activated carbon prepared by direct chemical activation of biomass (10 CS-ZP) and commercial mesoporous carbon. It can also be observed from FIG. 10 that the saturation capacities of CS-HHTZP, CS-ZP and commercial mesoporous carbon are 913 mg/g, 715 mg/g and 176 mg/g, respectively. Notably, the saturation capacity of mesoporous carbon, CS-HHTZP, is 28% higher compared to that of CS-ZP. This enhancement in adsorption again demonstrates the contribution of higher (15 mesoporosity that resulted from the hydrogen peroxide laden hydrothermal treatment prior to chemical activation.

The results demonstrate the significant advantageous effects of the hydrothermal pre-treatment step in the presence of hydrogen peroxide and its role in significantly increasing the mesopore area of the activated carbon produced. (20 Hydrothermal carbonization using hydrogen peroxide creates more oxygenated functional groups that promote facile chemical activation. The oxygenated functional groups (carboxylic, lactonic and phenolic) content in the precursor is an important indicator of reactivity which governs the chemical activation and thus can be used as a predictor of porosity in the activated carbons. The study demonstrates (25 the importance of surface modification of raw biomass waste in the formation of excellent precursors with increased OFG (oxygenated functional groups) content which is favorable for chemical activation and thus has a strong advantageous effect in the preparation of the mesopore areas of the resulting carbons. A significant increase in the mesopore area is achieved by complementing the chemical (30 activating agent with the oxidizing agent.

While specific compositions and parameters were detailed in the above example, it will be apparent to those of ordinary skill in the art that modifications and changes may be made therein without departing from the scope of the present invention.

5 As is evident from the foregoing discussion, the present invention provides a process to produce a hydrochar with increased oxygenated functional group content and an activated carbon with high or increased mesoporosity and surface area from waste biomass. Advantageously, incorporation of an oxidizing agent during hydrothermal treatment of the biomass induces the formation of oxygenated
10 functional groups (OFG) on the resultant hydrochar. The high or increased OFG content on the hydrochar facilitates formation of significantly high mesoporosity carbons following chemical activation.

The mesoporous carbons produced in accordance with the present invention are suitable for application in many fields such as, for example, energy storage,
15 water treatment, gas separation and purification, and electro-catalysis.

While preferred embodiments of the invention has been illustrated and described, it will be clear that the invention is not limited to the described embodiments only. Numerous modifications, changes, variations, substitutions and equivalents will be apparent to those skilled in the art without departing from the
20 scope of the invention as described in the claims.

Further, unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising" and the like are to be construed in an inclusive as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

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CLAIMS

1. A process for making activated carbon, comprising:
providing a biomass;
5 mixing the biomass with an oxidizing agent to form a biomass-oxidizing agent mixture;
subjecting the biomass-oxidizing agent mixture to a hydrothermal carbonization process to form a hydrochar having an increased oxygenated functional group content compared to that of the biomass;
10 mixing the hydrochar with an activating agent to form a hydrochar-activating agent mixture; and
subjecting the hydrochar-activating agent mixture to a chemical activation process to form an activated carbon.
- 15 2. The process for making activated carbon of claim 1, wherein the biomass comprises one or more of coconut shell, palm kernel shell, sawdust, wood, nut shell, husk, fruit pit, seed, peel, bagasse, peat, lignite and sub-bituminous coal.
- 20 3. The process for making activated carbon of claim 1, wherein the biomass is provided in the form of coarse granules having a particle diameter of between 0.5 millimetres (mm) and 5 mm.
4. The process for making activated carbon of claim 1, wherein the oxidizing agent comprises one or more of hydrogen peroxide, a carboxylic acid,
25 a peroxy acid, a dibasic acid and a humic acid.
5. The process for making activated carbon of claim 1, wherein the biomass-oxidizing agent mixture comprises between 60 percent by mass (wt%) and 80 wt% of the biomass.

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6. The process for making activated carbon of claim 1, wherein the hydrothermal carbonization process is performed at a temperature of between 200 degrees Celsius (°C) and 300 °C for a period of between 20 minutes (min) and 200 min.
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7. The process for making activated carbon of claim 1, wherein the hydrochar has between 30 percent (%) and 70 % more oxygenated functional group content than the biomass.
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8. The process for making activated carbon of claim 7, wherein the hydrochar has between 40 % and 60 % more oxygenated functional group content than the biomass.
9. The process for making activated carbon of claim 1, wherein the hydrochar has an oxygenated functional group content of between 1.2 milliequivalent per gram (meq/g) and 1.6 meq/g.
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10. The process for making activated carbon of claim 9, wherein the oxygenated functional group content is 1.29 meq/g, 1.42 meq/g or 1.58 meq/g.
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11. The process for making activated carbon of claim 9, wherein the oxygenated functional group content comprises one or more of a carboxylic group, a lactonic group and a phenolic group.
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12. The process for making activated carbon of claim 1, wherein the activating agent is one or more of zinc chloride, phosphoric acid, a metal chloride, an inorganic acid, sodium phosphate and a base.

13. The process for making activated carbon of claim 1, wherein a ratio of the activating agent to the hydrochar in the hydrochar-activating agent mixture is between 2:1 and 10:1.
- 5 14. The process for making activated carbon of claim 1, wherein the chemical activation process is performed at a processing temperature of between 350 °C and 650 °C for a period of between 0.5 hours (h) and 3 h.
- 10 15. The process for making activated carbon of claim 13, wherein the chemical activation process is ramped to the processing temperature at a rate of between 5 degrees Celsius per minute (°C/min) and 15 °C/min.
- 15 16. The process for making activated carbon of claim 1, wherein the chemical activation process is performed in a presence of nitrogen gas at a flow rate of between 20 millilitres per minute (ml/min) and 100 ml/min.
17. A process for making hydrochar, comprising:
providing a biomass;
mixing the biomass with an oxidizing agent to form a biomass-oxidizing
20 agent mixture; and
subjecting the biomass-oxidizing agent mixture to a hydrothermal carbonization process to form a hydrochar having an increased oxygenated functional group content compared to that of the biomass.
- 25 18. The process for making hydrochar of claim 17, wherein the biomass comprises one or more of coconut shell, palm kernel shell, sawdust, wood, nut shell, husk, fruit pit, seed, peel, bagasse, peat, lignite and sub-bituminous coal.

19. The process for making hydrochar of claim 17, wherein the biomass is provided in the form of coarse granules having a particle diameter of between 0.5 millimetres (mm) and 5 mm.
- 5 20. The process for making hydrochar of claim 17, wherein the oxidizing agent comprises one or more of hydrogen peroxide, a carboxylic acid, a peroxy acid, a dibasic acid and a humic acid.
21. The process for making hydrochar of claim 17, wherein the biomass-
10 oxidizing agent mixture comprises between 60 percent by mass (wt%) and 80 wt% of the biomass.
22. The process for making hydrochar of claim 17, wherein the hydrothermal carbonization process is performed at a temperature of between 200 degrees
15 Celsius (°C) and 300 °C for a period of between 20 minutes (min) and 200 min.
23. The process for making hydrochar of claim 17, wherein the hydrochar has between 30 percent (%) and 70 % more oxygenated functional group content than the biomass.
- 20 24. The process for making hydrochar of claim 23, wherein the hydrochar has between 40 % and 60 % more oxygenated functional group content than the biomass.
- 25 25. The process for making hydrochar of claim 17, wherein the hydrochar has an oxygenated functional group content of between 1.2 milliequivalent per gram (meq/g) and 1.6 meq/g.
26. The process for making hydrochar of claim 25, wherein the oxygenated
30 functional group content is 1.29 meq/g, 1.42 meq/g or 1.58 meq/g.

27. The process for making hydrochar of claim 25, wherein the oxygenated functional group content comprises one or more of a carboxylic group, a lactonic group and a phenolic group.