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Upcycling brewer's spent grain waste into activated carbon and carbon nanotubes via two-stage activation for energy and other applications

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Abstract

In this study activated carbon (AC) and carbon nanotubes (CNTs) were synthesised from Brewer's Spent Grain (BSG); a form of lignocellulosic biomass, more commonly known as barley waste. A novel approach involving two activation steps; firstly, with phosphoric acid (designated BAC-P) and then using potassium hydroxide (designated BAC-K) was proposed for the production of AC and CNTs from BSG. The AC produced showed a surface area as high as $692.3 \text{ m}^2.\text{g}^{-1}$ with a pore volume of $0.44 \text{ cm}^3.\text{g}^{-1}$. This can help aid and facilitate the circular economy by effectively up-cycling and valorising waste lignocellulosic biomass to high surface area AC and subsequently, multi-walled carbon nanotubes (MWCNTs). Consequently, MWCNTs were prepared from the produced AC by mixing it with the nitrogen-based material melamine and iron precursor, iron (III) oxalate hexahydrate, where it produced a hydrophilic multi-wall carbon nanotubes (MWCNTs). Both AC and CNTs materials were used in heavy metal removal (HMR), where the maximum lead absorption was observed for sample BAC-K with 77% removal capacity after the first hour of testing. This result signifies that the synthesis of these up-cycled materials can have application in the areas of wastewater treatment or other AC/CNT end uses with a rapid cycle time.

Keywords:

Brewer's Spent Grain, Biomass, Activated carbon, Carbon nanotubes, Pyrolysis, Activating agent, Multi-wall carbon nanotubes, Carbon nanoparticles.

Graphical abstract:

1. Introduction

There is an ever-increasing focus across all sectors on minimising industrial waste globally. One approach to this that is gaining considerable interest, is using biomass-based fuels ¹⁻³. The use of biomass can turn waste, which can be considered as a low-value material into usable energy or economically viable products such as waste from the distillery and brewing industry. The main form of biomass used in the brewing industry in Northern Ireland is barley. Over 144,400 tonnes were produced in Northern Ireland in 2017, making it the second most popular crop produced for 2017 and the most produced cereal crop ⁴. From the barley feedstock used in this industrial sector, Brewer's Spent Grain (BSG) is the main waste product. This specific waste stream and its volume is problematic for everyone. One such way of upcycling and providing end-use applications to barley waste is to act upon and facilitate the concept of the circular economy, which is deemed "regenerative by design" ⁵. The synthesis of value-added products from barley waste is a prime example, by taking a waste good and creating a high-value end product. This keeps materials such as intrinsic carbon inherent in biomass in use much longer than their original intended purpose. However, what we have promoted herein is a circular economy which starts as a biological waste (lignocellulosic biomass) then turned into a synthetic, long-lasting and resilient product (AC and CNTs). This provides benefits to the environment and society through economic and social opportunities. This circular economy will help reduce waste, raise resource productivity and create a more competitive economy. ^{5, 6} The reported composition of BSG showed it contained hemicellulose, cellulose and lignin of 34-48, 19-21 and 11-13%, respectively ^{7,8}. Furthermore, the extractives were in the range of 13-35%. The calorific value of the BSG has been found to be in the range of 19-22 MJ.kg⁻¹ ⁹⁻¹¹.

Pyrolyzing the BSG after it has dried is the next step in the potential process. Pyrolyzing the biomass is known to produce char, oil and vapour products. The char is the product that holds the potential to make the high-value products. The main variables that dictates which of these three products is

formed and the composition of the product formed is the original feedstock material, the temperature used in the pyrolysis process alongside the heating rate used. The synthesised char produced a high calorific value of 25.97 MJ.Kg⁻¹. This can, therefore, be applied in industrial heating applications (combustion or co-combustion) in furnaces and boilers. The nitrogen content was also seen to increase after the pyrolysis, thus biochar could be used as a potential soil amendment for soil fertility^{9, 10}.

Activated carbon (AC) has a string of properties that makes it incredibly interesting in the chemical world today. The main one is its tendency to have a large surface area. which can provide a huge potential for the adsorption of chemical compounds or the complete removal of them from already existing systems. There are two main routes for the formation of AC, using physical or chemical activation. The former involves a carbonisation step through pyrolysis at high temperature, followed by an activation or oxidation step where the sample is exposed to high temperatures in oxidising atmospheres. The latter method is through chemical activation which prior to carbonisation, the sample is impregnated with an activating agent, such as an acid, strong base or salt and then carbonised at a lower temperature than the physical activation. The pyrolysis temperature significantly influences the porosity of the AC, where higher temperatures of 800 °C produced a highly microporous carbon, while lower temperatures of 400-600 °C produced a mesoporous structure¹². As the temperature of the pyrolysis increased, the weight loss increased due to the release of volatile matter and carbon burn-off through carbon-steam oxidation due to the activating agent used. Demiral et al.¹³ reported that a temperature of 500 °C was the optimum temperature that would yield the best results in the activation pyrolysis. The step in the process that will bring about the biggest variety of products and which will determine the effectiveness of the AC is the activating agents used. Bachrun et al.¹⁴ used barley straw as a medium to produce activated carbon with a physical activation step using carbon dioxide.

A variety of activating agents have been used, with phosphoric acid being the most common along with potassium hydroxide, zinc chloride and sulphuric acid. Sahira et al.¹⁵ used different activating agents (KOH, H₂SO₄, FeCl₃, MgCl₂ and CaCl₂), and found out that the different activating agents have no significant effect on the nature of surface functional groups, with all showing similar oxygenated functional groups in FT-IR such as hydroxyl, carbonyl, carboxyl and lactones.

As mentioned, the use of phosphoric acid is one of the most commonly used activation agents. Romero-Anaya et al.¹⁶ used H₃PO₄ to produce a well developed mesoporous AC from banana biomass, with a high surface area of over 2000 m².g⁻¹ and a yield of over 35%. This is backed up by Quesada-plate et al.¹⁷ whom also used H₃PO₄ to produce AC of a high surface area or over 2000 m².g⁻¹ and high porosity, where H₃PO₄ promotes the fixing of carbon atoms onto the char from the banana biomass, thus, H₃PO₄ can be a lucrative activating agent for AC production and therefore it shall be explored herein. The use of an activating agent does not have to be restricted to one step. Once a char has been mixed with an activating agent and pyrolyzed, it can further be activated using a second activating agent. Ravichandran et al.¹⁸ reported that a two-step activation of the biomass could produce a higher adsorption AC with greater performance than a single activation AC. Compared to a one-step activation, the two-step activation was found to produce AC with up to 25% higher carbon yields. Also, the surface area increased by over 50% as well as the pore volumes increasing. Sahira et al.¹⁵ reported that AC impregnated with KOH showed well developed porous structure compared to other ACs prepared. Lua and Yang gave a comparison of the surface area between ACs from different biomass samples using KOH as the activating agent¹⁹. The surface areas that can be produced ranged from approximately 2400 m².g⁻¹ and lows of below 1 m².g⁻¹. For instance, oil-palm, coconut, pistachio-nut and macadamia shells were of 1408, 2451, 1946, 1600 m².g⁻¹, respectively.

The formation of Carbon Nanotubes (CNTs) is tubular structures made of carbon atoms, having a diameter in nanometres but a length in micrometres. CNTs possess many properties that make them

highly valued and sought after; such as high strength comparable to steel, electrical and thermal conductivity, stiffness and toughness and they have a wide range of applications in different industries ²⁰⁻²⁴. There are different methods to produce CNTs including Chemical Vapour Deposition (CVD), Arc Discharge, Laser Ablation and the other less explored methods such as Pyrolysis ²⁵. Yao et al.²⁶ prepared CNTs using melamine and iron salts produced N-doped CNTs from waste biomass (stillage residue, liquor industry waste) with the S_{BET} of the AC and the produced CNTs of approximately 1600 and 600 m^2g^{-1} , respectively.

In the literature, using two-step activation, the biomass is firstly carbonised at 800 °C, then activated using an activating agent (KOH, H_3PO_4 or ZnCl_2). For instance, Ravichandran et al. ¹⁸ reported that the biomass was pre-carbonised at 300 °C then activated with one of the three activating agents and then pyrolyzed at 700 °C which resulted activated carbon of 548 m^2g^{-1} . They primarily focused on the % AC yield. Basta et al. ²⁷ studied also the two-step activation method where the biomass was firstly carbonised at 800 °C, followed by chemical activation using KOH and finally pyrolyzing at 800 °C. Herein, we used a moderate pyrolysis temperature of 500 °C prior to our first chemical activation step of H_3PO_4 , one of two activating agents where KOH was used in the second activation step. This effectively changed the conventional sequence of experimental steps. Herein, we increased the H_3PO_4 : biomass ratio from 1:4 in the literature to 2:1, to increase the functionality of the biomass allowing more C-O-P bonding within the first activation step. Then in the second activation step using KOH, the penetrated free K atoms (intercalated K) will allow the expansion of the carbonaceous structure which can be removed easily by washing. The resultant ACs allow the formation of novel hydrophilic MWCNTs materials, as the literature mainly details production of hydrophobic CNTs materials. This might be due to the first activation step using H_3PO_4 , that helped the functionalisation of the carbonaceous material prior to pyrolysis, where conventionally the first pyrolysis step in literature leads to hydrophobic materials. Thus herein, to the best of the authors' knowledge, this is the first detailed study of using a two-step chemical activation method

on potato peel waste and goes beyond, to prepare hydrophilic MWCNTs materials and studies their applications in HMR.

1. Materials and methods

In processing the BSG, the first major step is immediate drying or refrigeration of the sample to prevent inevitable microbial degradation ²⁸, where the high moisture content, 67-81wt.% makes it highly susceptible to microbial activity and degradation ²⁹. This also shows that the BSG must have appropriate storage regimes in place downstream, prior to any processing or pre-processing that will take place. With the first step being drying, there are two main processes that can be considered. Santos et al. compared the difference in oven and freeze-drying, where the former was found to be the method of lowest economic cost. However, it does give rise to a small decrease in protein and fat content in comparison to the frozen sample ³⁰. The loss in content, however, is outweighed by the financial gains, especially, when considering the vast quantities of BSG that can be processed.

2.1 BSG sample

The BSG was collected from Bushmills Distillery in Bushmills, County Antrim, Northern Ireland, UK. The sample was immediately dried to avoid accelerated degradation as BSG is susceptible to microbial degradation due to its high moisture content. The sample was dried for 3 days at 105 °C removing the moisture content. A portion of the sample was ground using a mortar and pestle and sieved to 106 µm for further characterisation and heavy metal removal tests.

2.1.1 Activated carbon preparation

The production of AC was carried out via two consecutive activation methods as follows:

Scheme 1: The schematic procedure for the preparation of activated carbon and carbon nanotubes from Brewer's Spent Grain waste.

2.1.1.1 First activation with phosphoric acid

The specific weight of 11.4g of BSG was mixed with H₃PO₄ (activating agent) and 150 mL of deionised water. The mixture was then heated to 86 °C using a hot plate and mixed continuously for 2 hrs, then dried in an oven overnight at 110 °C. The dried sample was then added to a fixed bed reactor purged with a N₂ flow rate of 100 mL.min⁻¹. The heating regime consisted of ramping at a rate of 2 °C.min⁻¹ up to a temperature of 500 °C, then maintained for 30 mins and allowed to cool to room temperature. The sample was then washed with deionised water to remove excess acid and dried in an oven to remove moisture content from washing. The activated carbon produced was designated as BAC-P.

2.1.1.2 Second activation with potassium hydroxide

The BAC-P (3.12 g) was then mixed with KOH, added in the ratio of BAC-P: KOH, 1:3.5, then heated and stirred at 86 °C for 2 hours. The sample was then dried in an oven overnight then pyrolyzed at a constant heating rate of 4 °C.min⁻¹ up to 500 °C at 100 mL.min⁻¹ flow rate of N₂ maintained for 30 mins and allowed to cool to room temperature. These steps were then followed

by a sample washing with HCl solution to remove KOH and then hot water to neutralise pH. The sample was then dried to remove moisture from water washing. The activated carbon produced was designated as BAC-K.

2.1.2 Carbon nanotubes preparation

The final BAC-K produced in the second activation step was used as a carbon source in the preparation of the CNTs along with melamine (2,4,6-triamino-1,3,5-triazine, 99%, Sigma-Aldrich, UK) and iron (III) oxalate hexahydrate ($\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, UK) and mixed in methanol (HPLC grade, $\geq 99.9\%$, Sigma-Aldrich, UK) and then stirred for 4 hrs before washing with deionised water and drying in the oven at 80 °C overnight. This step involved two-stage pyrolysis of the three-component mixture (BAC-K, melamine and iron (III) oxalate hexahydrate), ramped up to 600 °C at a heating ramp of 2 °C.min⁻¹ and then held for 3 hrs before being subsequently pyrolysed to 900 °C at 2 °C.min⁻¹ and held for an hour, then cooled down to room temperature. The carbon nanotubes produced was designated as CNTs.

2.2 Lignocellulosic biomass Characterisation

Powder X-ray diffraction (XRD) was carried out using a PANalytical X'Pert Pro X-ray diffractometer. This diffractometer was equipped with a CuK_α X-ray source with a wavelength of 1.5405 Å. The diffractograms were collected up to $2\theta = 80^\circ$. The X-ray tube was set at 40 kV and 40 mA.

Brunauer-Emmett-Teller (BET) analysis was performed using a Micromeritics ASAP 2020 system. BET surface area and pore volume were measured by N₂ adsorption and desorption isotherms at liquid nitrogen temperature (-196 °C).

Scanning Electron Microscopy (SEM) was carried out on a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT Microscope Control software and linked to an energy-dispersive X-ray (EDX) detector. Two types of detectors were used in SEM analysis;

the Everhart-Thornley Detector (ETD) which is used to detect secondary electrons emitted from the sample and Back-Scattered Electron Detector (BSED). The EDX used was a 10 mm² silicon drift detector (SDD)-x-act from Oxford Instruments which utilises Aztec® EDS analysis software. Both systems used the same chamber.

The static contact angle of the catalyst pellets with water was measured using a contact angle meter equipped with a CCD camera (FTA1000 Drop Shape Instrument- B Frame system).

The composition of the BSG sample was characterised by means of proximate and ultimate analyses. Elemental (C, H and N) Analysis was performed using a Perkin Elmer PE2400 CHNS/O Elemental Analyzer. The oxygen content was calculated by difference from the data obtained by a Perkin Elmer PE2400 CHNS/O Elemental Analyzer machine.

TGA was performed from 50 to 800-1000 °C with multiple heating rates of 2, 5, 15, 25 and 50 °C.min⁻¹, in a stream of dry N₂ flowing at 20 cm³.min⁻¹, using a simultaneous thermal analysis Mettler Toledo (TGA/DSC) Thermogravimetric analyzer Pyris TGA/DSC1. Changes in mass of the sample were recorded during the ramping operation.

Fourier Transform Infrared (FT-IR) spectroscopy was operated using a Perkin Elmer Spectrum, a beam splitter in the wavenumber range of 4000 – 400 cm⁻¹.

The morphology of the catalysts' surface was characterised by transmission electron microscopy (TEM) (JEOL 2100 with high tension of 200 kV and a point resolution of 0.24 nm). XPS was performed in a ThermoFisher Scientific Instruments (East Grinstead, UK) with a quartz monochromator Al K α radiation of energy 1486.6 eV. For construction and fitting of synthetic peaks of high-resolution spectra, mixed Gaussian-Lorentzian functions with a Shirley-type background subtraction were used.

3. Results and Discussion

3.1 Lignocellulosic biomass characterisation

3.1.1 XRD analysis

The XRD analysis gives an indication of the crystalline structures present in the sample, thus allowing identification of components such as cellulose; one of the main constituents of biomass samples. Cellulose crystallinity can be in the form of amorphous (diffraction lines at $2\theta = 18^\circ$) or crystalline (diffraction lines at $2\theta = 22^\circ$ corresponding to the crystallographic plane (002) with JCPDS data 03-0289), while both hemicellulose and lignin are known to be amorphous in nature¹⁸.

The first activation of BSG using phosphoric acid has resulted in compromised activated carbon. Girgis et al.³¹ show that the XRD analysis for H_3PO_4 treated activated carbon contains diffractions at $2\theta = 23, 26$ and 27° . The second activation has two main diffractions of the graphite phase at $2\theta = 24$ and 43° . This signifies that the biomass has shifted towards a regular crystalline structure³². The residual impurities from the previous activation have been removed as shown in the XRD analysis, this may be due to KOH reacting with any residual H_3PO_4 and the activation removing any residual impurities. Although KOH is used as an activating agent, it can also be used in the acid-base reaction with any excess H_3PO_4 in the activated carbon, after washing these salts and impurities would be removed. The XRD analysis of the final product confirms the presence of carbon nanotubes by the diffractions at $2\theta = 26$ and 43° .

Figure 1: XRD patterns of samples of activated carbon derived from barley waste using firstly phosphoric acid (BAC-P), and secondly using potassium hydroxide (BAC-K) alongside the Carbon nanotubes (CNTs).

3.1.2 S_{BET} analysis

Brunauer-Emmett-Teller (BET) analysis was carried out to measure the surface area and the pore volume of the original BSG samples along with the produced ACs and CNTs. It is not surprising that the surface area of the BSG sample was significantly low at $1.23 \text{ m}^2.\text{g}^{-1}$, while this dramatically increased to 497.4 and $692.3 \text{ m}^2.\text{g}^{-1}$ for BAC-P and BAC-K, respectively. This is in line with the increase in the pore volume which was only $0.002 \text{ cm}^3.\text{g}^{-1}$ for the BSG sample, while BAC-P and BAC-K were found to have a pore volume of 0.285 and $0.440 \text{ cm}^3.\text{g}^{-1}$, respectively. Interestingly, the increase in the surface areas from the first activation method to the second activation method is in agreement with the XRD results. This signified the removal of impurities by the second activation method which might have removed impurities and helped to create more pores in the surface of the

activated carbon. Also, the pore volume in the second activation method increased by 64.8% compared to the first activation method as shown in Table 1. The CNTs showed a surface area of $64.4 \text{ m}^2.\text{g}^{-1}$, implying that the CNTs formed are Multi-Walled with 30-40 walls present with a nanotube diameter of approximately 30 nm³³. The formation of MWCNTs has advantages over SWCNTs in terms of enhanced chemical and thermal stability. The surface properties of MWCNTs can also be preserved better than SWCNTs, due to only the outer layer being exposed to chemical modifiers³⁴.

Figure 2: The adsorption/desorption isotherms of the activated carbons derived from barley waste using firstly phosphoric acid (BAC-P), and secondly using potassium hydroxide (BAC-K).

The elemental analysis (CHNS) of BSG, BAC-P, BAC-K and CNTs showed that the wt.% of carbon increased from 49 wt.% (BSG) to around 70 wt.% (BAC-P, BAC-K and CNTs) as shown in Table 1. On the other hand, wt.% of nitrogen decreased from 2.58 wt.% for BSG to around 0.3 wt.% for the different ACs (BAC-P and BAC-K), then increased to 7 wt.% for the CNTs due to the presence of melamine (contains 67 wt.% nitrogen) during the preparation of CNTs. In a similar trend, the wt.% of iron in the CNTs showed 5.9 wt.% due to the presence of iron oxalate as seen from the EDX results in Table 1. The average wt.% of carbon reported for BSG was 49.50%, where the lower and the higher wt.% reported were 46.6 and 51.6%, respectively ^{7, 10, 11}. The hydrogen wt.% reported herein is in agreement with that in the literature which was in the range of 6.4-6.8% ^{7, 8, 10}. The nitrogen and sulphur wt.% reported herein as 2.6 and 0.3 wt.%, respectively, is slightly lower than that reported in the literature of 3.5 and 0.7 wt.% for nitrogen and sulphur, respectively ^{8, 10}.

Table 1: Physicochemical characterisations of brewer's spent grain (BSG) along with the ACs (BAC-P, BAC-K) and CNTs samples.

Samples		BSG	BAC- P	BAC-K	CNTs
<i>Elemental composition</i> (wt.% on dry basis)	% C	49.06	70.61	70.37	70.79
	% H	6.54	3.42	1.44	1.67
	% N	2.58	0.34	0.2	7.67
	% S	0.3	0.1	0.1	0.1
	% O	41.52	25.53	27.89	19.77
<i>EDX analysis</i> (wt.% on dry basis)	C	62.3	77.0	83.0	84.7
	O	36.9	18.2	16.8	9.4
	Si	0.7	0.7	0.2	--
	P	<0.1	4.1	--	--
	Fe	--	--	--	5.9
<i>S_{BET} results</i>	S_{BET}(m².g⁻¹)	1.2	497.4	692.3	64.4
	Pore volume (cm³.g⁻¹)	0.002	0.285	0.440	0.05

3.1.3 SEM-EDX analysis

The SEM images of BAC-P, BAC-K and CNTs using the ETD detector are shown in Figure 3. The first method activated carbon using phosphoric acid showed a fascicular and rods structure morphology as shown in Figure 3 (a). Interestingly, the surface morphology was significantly changed during the second activation method (KOH) and it is obvious that KOH helped to open up the surface structure and improve the porosity as shown in Figure 3 (b). This result is in line with the XRD and SBET results, which showed lower impurities and higher surface and pore volume during the second activation process compared to the first activation step as shown in Figure 1, 2 and Table 1. The final preparation step of synthesising CNTs from ACs (BAC-K) is shown in Figure 3 (c), where the CNTs are shown at a higher magnification level compared to the ACs.³⁵

Figure 3: SEM images for Barley ACs along with CNTs a) H_3PO_4 activation (BAC-P), b) KOH activation (BAC-K) and c) CNTs at different levels of magnification using ETD detector.

3.1.4 TGA/DTG analysis:

The thermal decomposition of BSG at multiple heating rates (2.5, 10, 20 and 30 °C.min⁻¹) along with CNTs are shown in Figure 4. It is well known that hemicellulose and cellulose decompose between 200-375 °C and 275-380 °C, respectively, while lignin is decomposing over a wide range of temperatures (180-550 °C) ^{36, 37}. In general, the thermal decomposition was in the temperature range of 225-637 °C, which is a wider temperature range than that reported by Balogun et al.⁹ of 327-600 °C. It is obvious that there are two decomposition stages as shown from the DTG curves of the BSG in Figure 4 (a). This is in agreement with the work published by Vanreppelen et al. and Mahmood et al. ^{7, 8} who showed that there are two significant weight loss peaks at 281 and 341°C whereas, herein it was 280 and 343 °C. Protásio et al.³⁸ reported that the first decomposition peak related to the energy released by the decomposition of cellulose and hemicellulose in volatiles, while the second peak can be assigned to the decomposition of fixed carbon and residual lignin. The decomposition peaks shifted toward higher temperature by increasing the heating rate; as the heating rates increased from 2.5 to 30 °C.min⁻¹, the first and second decomposition peaks shifted by 49 and 34 °C, respectively.

The char yield that was produced in pyrolysis process at a lower temperature (450 °C) was more than twice that of higher temperature (800-850 °C) of 52.5 and 23.5%, respectively ^{7, 8}. The resulted char or biochar has a higher calorific value than the original BSG due to an increase in fixed carbon and carbon content ⁹. The reported calorific values of biochar of 25.97 MJ.kg⁻¹ and 25 MJ.kg⁻¹ provide the potential to be turned into more value-added products along with offering a suitable fuel source ^{9, 10}. The thermal decomposition of the CNTs is shown in Figure 4 (b), where it showed 38.1% of weight loss in the temperature range of 509-709 °C. This is in agreement with the work done by Su et al. who reported around 36% weight loss for Multi-Walled Carbon Nanotubes ³⁹.

The ignition and burnout temperatures along with the heat liberated of BSG at different heating rates were calculated from the DSC curves and presented in Figure S1 and Table 2. There was a

32°C increase in the ignition temperature with increasing the heating rates from 1 to 8 °C.min⁻¹ and this is in agreement with the work done by Kok and Ozgur⁴⁰. On the other hand, the burnout temperature increased three times that of the ignition temperature by 97 °C with increasing the heating rates by the same value. The heat liberated at 1 °C.min⁻¹ was 241.8 (W.g⁻¹) and significantly increased with increasing the heating rate to 8 °C.min⁻¹ to reach 1405.1 W.g⁻¹ as shown in the supplementary information (Figure S1) and Table 2.

Table 2: Calculated ignition and burnout temperatures along with the heat liberated during the combustion of Brewer's Spent Grain (BSG) under air atmosphere.

Heating rates	Heat liberated (W.g-1)	Ignition temp. (°C)	Burnout temp. (°C)
1	241.8	222	553
2	320.3	237	583
4	748.6	241	623
8	1405.1	254	650

Figure 4: Thermogravimetric analysis of Brewer's Spent Grain at different heating rates: a) TGA/DTG curves of BSG and b) TGA/DTG curves of CNTs.

The thermal decomposition of lignocellulosic biomass starts with the depolymerisation and thermal cracking of the functional groups of hemicellulose (150-250 °C) as reported by Zapata et al.⁴¹. Then followed by the defunctionalisation, depolymerisation and chain-breaking of cellulose (250-360 °C) and finally lignin degradation (380-585 °C). In a recent study, pyrolysis of the three lignocellulosic biomass materials was performed in a fixed bed reactor, the mass spectrometer (MS) results showed release of main emissions such as N₂O (180-340 °C), H₂O (200-380 °C) and two large H₂ peaks (580 and 700 °C). Furthermore, traces of emissions were also reported such as CO₂, acetic acid, hydrocarbons (methane and ethane), methyl alcohol and traces of other nitrogen oxides (NO and NO₂)⁴². Furthermore, it was reported that the pyrolysis of biomass N and coal over 300°C releases emissions of NH₃ (850°C), HCN⁴³⁻⁴⁵ (700-1000 °C) and isocyanic acid (HNCO > 600 °C) using two stages set up, with a fluidised bed reactor followed by a tubular flow reactor⁴⁶. All the emissions reported above should be considered when reporting on the circular opportunities of waste biomass source such as BSG.

3.1.5 TEM analysis:

The barley activated carbons (BAC-P and BAC-K) and the synthesised carbon nanotubes (CNTs) TEM images are shown in Figure 5 (a-c). The surface morphology of the BAC-P and BAC-K is amorphous multilayer, which is in agreement with the S_{BET} and SEM results in Figure 2 and 3. It is obvious that the CNTs in Figure 5 (c) are less than 20 nm. Interestingly, the S_{BET} result of the CNTs was 64.4 m².g⁻¹, where there is a relationship between the surface area of the CNTs and the wall thickness. For example, such a high surface area of 1375 m².g⁻¹ is attributed to the maximum theoretical prediction of a single wall CNTs (SWCNTs), whereas MWCNTs tend to have surface areas in the range of 15-500 m².g⁻¹. Where the surface areas of 500, 175 and 50 m².g⁻¹ correspond to 3-walled (6 nm in diameter), 10-walled (15 nm diameter) and 40-walled (35 nm diameter), respectively. Given the surface area herein, it is apparent that the CNTs are MWCTs with 10-40 walls and 15-35 nm diameter⁴⁷. The lower surface area of the CNTs could be due to multilayer

polygonal particles and large graphite platelets, the presence of amorphous carbon particles and impurities ⁴⁸. It is worth noting that the formation of MWCNTs has advantages over SWCNTs due to its thermal stability, the enhanced chemical and low product cost per unit ³⁴.

Figure 5: TEM images for a) activated carbon (BAC-P), b) activated carbon (BAC-K) and c) CNTs.

3.1.6 XPS analysis

The XPS analysis was performed on the activated carbon (BAC-P) and the CNTs to detect the composition and oxidation states of the surface species along with the binding energies as shown in Figure 6 (a-g) and Table 3. The *C1s* peak for both of them was mainly at the binding energy of 284.4 eV (C-C), while CNTs showed a small peak at around 288 eV which is attributed to the C=O in the carbonyl group of the CNTs structure or N-C=O in the N-doped carbon structure of the CNTs⁴⁹. The at.wt.% of carbon slightly increased from BAC-P to CNTs as shown in Table 3, however, O1s significantly decreased from 17.5 to 4.2 at.wt%, respectively, implying that the oxide species decreased during the formation of carbon nanotubes and shifted from C-O in the AC structure to C=O in the CNTs structure as seen in Figure 6 (b)⁵⁰. It is not surprising that the *P2p* peak disappeared during the transformation of activated carbon into CNTs, where only BAC-P showed a peak of *P2p_{1/2}* at a binding energy of 133 eV which is attributed to C-O-P bonding in the AC structure as seen in Figure 6 (c). On the other hand, a small peak of *Fe2p* appeared in the CNTs due to the presence of iron oxalate during the preparation of CNTs. The CNTs showed a peak of *Fe2p_{3/2}* at a binding energy of 711.3 eV which is attributed to γ -Fe₂O₃ phase (Figure 6 (e)), which is in agreement with the reported MWCNTs structures in the literature⁵¹. The CNTs showed another new peak of *N1s* at binding energy of 398.2 eV which is attributed to one of the three main constituents of nitrogen-doped sp² carbon material system, which contributes to the pyridinic N atom which bonds with two C atoms at the edges or defects of graphene and contribute one p electron to the π system)^{52, 53}. The XPS survey (Figure 6(g)) for both of BAC-P and CNTs looks comparable apart from the appearance of extra peaks of *N1s* and *Fe2p* along with the absence of *P2p* during the transformation of barley activated carbon into CNTs.

Figure 6: XPS of Barley activated carbon, BAC-P (dash line) and CNTs (solid line) of a) C 1s, b) O 1s, c) P 2p, d) Na 1s, e) Fe 2p, f) N 1s and g) survey.

Table 3: XPS results of the activated carbon BAC-P along with the CNTs sample.

SAMPLE	C1s		O1s		N1s		Si2p		P2p		Fe2p	
	Peak B.E.	Atomic wt. %	Peak B.E.	Atomic wt. %	Peak B.E.	Atomic wt. %	Peak B.E.	Atomic wt. %	Peak B.E.	Atomic wt. %	Peak B.E.	Atomic wt. %
BAC-P	284.4	82.0	532.5	17.2	--	--	--	--	133.3	0.6	--	--
CNTs	284.4	83.5	530.8	4.2	398.6	10.9	101.5	0.4	--	--	710.8	1.0

3.1.7 The water contact angle and FTIR analyses

The BSG and the synthesised CNTs water contact angle in θ are shown in Figure 7 (a, b) to measure the surface hydrophilicity as shown by Young's equation (Eq. 1)

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

Where, γ_{SV} , γ_{SL} and γ_{LV} stand for the interfacial surface tension of solid (S), liquid (L) and gas vapour (V). The value of θ gives an indication of the surface wettability where it can be classified into four different categories; super-hydrophilic ($\theta < 10^\circ$), hydrophilic ($10 < \theta < 90^\circ$), hydrophobic ($90 < \theta < 150^\circ$) and super-hydrophobic ($\theta > 150^\circ$). The water contact angle of BSG of $\theta = 47.12^\circ$ showed that the dry basis of barley used herein is hydrophilic as shown in Figure 7 (a). The water contact angle of both ACs deceased to 29.48° and 27.60° for BAC-P and BAC-K, respectively as shown in the supplementary information (Figure S2). Furthermore, the contact angle significantly decreased ($\theta = 13.35^\circ$) in the case of CNTs, implying that the produced CNTs in fact, are more hydrophilic than the raw materials (BSG) as shown in Figure 7 (b). This is in line with the literature, where hydrophilic CNTs were prepared with a contact angle in the range of $7.0 - 12.5^\circ$ ⁵⁴.

Figure 7: The water contact angle analysis of BSG (a) and the produced CNTs (b) along with the FT-IR of the BSG (c) and CNTs (d).

The FTIR spectra of the BSG and CNTs are shown in Figure 7 (c, d). The major absorption bands for BSG (Figure 7 (c)) are 3350, 2945-3000, 1251, 1450 and 1130 cm^{-1} , which correspond to O-H stretching, C-H symmetrical stretching, C-H plane bending vibrations, C=O bending and C-O-C stretching, respectively^{55, 56}. All of these are indicative of the cellulose fingerprint region. The double bands at 2945 and 3000 cm^{-1} are both indicative of cellulose as well as the band at 1450 cm^{-1} due to the C-H stretching. The C-O-C stretching band at 1130 cm^{-1} attributed to the presence of esters within the barley indicative again of the cellulose presence.

Figure 7 (d) shows the FT-IR spectra of CNTs where the major band shown at 3400 cm^{-1} is attributed to stretching of O-H bonds implying a hydrophilic material. The absorption band attributed to the carbon bonding in MWCNTs i.e. C=C are shown at $1620\text{-}1635\text{ cm}^{-1}$. The carbonyl group (C=O) is also shown at 1742 cm^{-1} ⁵⁷⁻⁵⁹. The broad water band at 3400 cm^{-1} showed that the produced CNTs is hydrophilic which is in agreement with the results of water angle results shown in Figure 7 (b). It is not surprising that the water absorption band in CNTs is larger than that of BSG sample as the water angle test showed that the produced CNTs is more hydrophilic than the BSG sample.

3.2 Heavy metal removal results:

The use of AC has been researched extensively ^{60, 61} and as the surface area and pore volume of the activated carbon increases, its use in heavy metal removal also increases. Al-Malek et al. ⁶⁰ could remove 94% of lead ions from an aqueous solution at optimum conditions when using AC. El-Zayat et al. ⁶² used biomass produced AC to remove lead, copper and cadmium up to 97%, 95% and 80% respectively. A few works have been carried out for the conversion of Barley waste into activated carbon or further into carbon nanotubes. Osasona et al. ⁶³ prepared ACs using a single-step acid activation from barley husks to be used to adsorb cadmium from aqueous solutions, however, the surface area along with the pore volume was not reported.

One such potential use of ACs and CNTs is in HMR from wastewater, where both were used herein to remove the Pb^{2+} ion as a common heavy metal in wastewater ⁶⁴. Figure 8 showed that after one hour of the test, the Pb^{2+} adsorption capacities were as follows: BAC-K > CNTs > BAC-P with adsorption values of 77, 35 and 33%, respectively. It is not surprising that BAC-K showed the highest rate of heavy metal absorption as shown in Figure 2 and Table 1. These results are in agreement with the S_{BET} results which showed that BAC-K offered the highest surface area and pore volume among the prepared samples. The BAC-K sample removed 96% of Pb^{2+} after 72 hours of the test, where BAC-P and CNTs removed 90 and 77%, respectively. Although the CNTs showed

the lowest removal rate based on a longer timeframe, it still removes 89% of Pb^{2+} over 7 days, thus showing a high adsorption capacity. The lowest HMR of the CNTs may be due to the lower surface area along with the pore volume.

Figure 8: The heavy metal removal test of lead on BAC-P, BAC-K along with the CNTs over a 168-hour timeframe.

The SEM/EDX of the lead activated carbon (BAC-K spent sample) along with the elemental mapping of Pb and C are shown in Figure 9. The EDX result shows the wt.% composition of the lead BAC-K with 77.2, 20.4 and 2.2 wt.% for C, O and Pb, respectively, as shown in Figure 9a. The elemental mapping in Figure 9c, 9d show that carbon is dominating the surface of the barley activated carbon (BAC-K), compared to the lead-heavy metal. This result confirms that some of the lead was adsorbed on the surface of the BAC-K sample.

Considering the circular process, the spent activated carbon after the adsorption of heavy metals should be regenerated in a green and sustainable way otherwise, it would turn into hazardous waste. Moreover, during the preparation of the activated carbon and CNTs, the amount of water used should be considered as well.

Figure 9: SEM- EDX analysis of barley lead activated carbon a) EDX results b) ETD image, c) carbon map and d) lead map.

4. Conclusion

In this study BSG; a type of lignocellulosic biomass was used for the production of activated carbon by means of two different activation steps. The first activation method using phosphoric acid (BAC-P), created a porous activated carbon with a surface area of $497.4 \text{ m}^2.\text{g}^{-1}$ and a pore volume of $0.285 \text{ cm}^3.\text{g}^{-1}$. This was a substantial increase and added value for the material compared to the parameters of BSG. This activated carbon was further treated using a second method which used potassium hydroxide as the activating agent (BAC-K). This allowed a further increase in the surface area and pore volume which were found to be $692.3 \text{ m}^2.\text{g}^{-1}$ and $0.44 \text{ cm}^3.\text{g}^{-1}$, respectively. Finally, the CNTs that were produced using BAC-K were found to be hydrophilic and be of the multi-walled type (MWCNTs). This was identified by the contact angle of $\theta = 13.35$. Subsequently, the two activated carbon samples and the CNTs produced were tested in the application of heavy metal removal (HMR) with the potential to remove up to 77% of lead within the first hour of operation. Of these materials tested BAC-K was the best and most suitable in HMR, making it the ideal candidate in the rapid removal of heavy metals in wastewater treatment or in alternative adsorption applications. The novel route outlined to high surface area ACs and hydrophilic MWCNTs from this particular waste stream helps address and apply the circular economy concept by up-cycling an otherwise, waste feedstock by adding value and other potential routes for application such as wastewater treatment and other end uses for AC and CNTs.

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