



Pyrolysis or hydrothermal carbonisation for anaerobic-digested sewage sludge? A comparison of pyrochar and hydrochar structure and stability

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Abstract

Thermochemical conversion of sewage sludge was proven as a useful method for waste management. Moderate temperatures in the absence of oxygen (pyrolysis) and hydrothermal carbonisation (HTC) performed in the presence of water, under autogenous pressures, were selected to treat the same sample of anaerobic-digested sewage sludge (SS). Two hydrochars were prepared by HTC in one high-pressure reactor using SS at 80% humidity content and heating it at 180 and 240 °C for 4 h, leading to H180-4 and H240-4, respectively. Two pyrochars were prepared from a pre-oven-dried SS at 105 °C for 48 h, followed by slow pyrolysis at 300 °C for 1 h, and 400 °C for 1 h leading to P300-1 and P400-1, respectively. HTC and slow pyrolysis significantly increased thermal stability of chars with higher temperatures, only reducing organic matter content (from 68.4 to 46.7–59.2%). Based on the characterisation results, the treatments could be a suitable choice to pre-treat sludge as soil amendment. Higher temperatures of pyrolysis would be attractive to store stable carbon in soil and construction materials, whilst lower temperatures of pyrolysis and HTC would produce a material that could be used as a source of organic matter providing a pool of labile carbon and fixed carbon. Thermochemical conversions generated mesopores (10–50 nm, >40%) and slightly increased surface area from 2 m²/g (SS) to 5–17 m²/g (pyrochars) and to 20 m²/g (hydrochars). Hence, HTC showed the greatest potential to produce a material with higher adsorption capacity (100 cm³/g for H180-4) but all chars should be subjected to an activation process to be able to compete with other kinds of feedstocks. The reduction of the H:C and O:C from the original SS after the treatments indicated a greater carbonisation degree, but a general reduction of the high heating value (HHV) from 17.94 MJ kg⁻¹ in SS to (14.93 MJ kg⁻¹). The torrefied char and hydrochars could be an attractive option to reduce energy of the process and drying stage in the case of HTC.

Keywords Sewage sludge · Biosolids · Hydrothermal carbonisation · Lower classed biochar · Pyrochar · Hydrochar

1 Introduction

Due to their high concentration in organic matter and essential plant nutrients (N-P-K) [1], digesting and composting sewage sludge for agricultural use remains the main route of management in Europe [2]. However, the increasing amounts of sewage sludge produced, their greater diversification, variability, and complexity of its components are a current cause of concern [3]. Considered a biohazardous waste, as it contains the pollutants removed from the waste water (from heavy metals, to fatty acids, a wide range of microorganisms including pathogens, microplastics, and other trace materials), sewage sludge management constitutes a logistic challenge aggravated by their significant water content which translates in greater volumes [4, 5]. Up until recently, heavy metal content had been the greatest limitation for their use in

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soil (Directive 86/278/EEC) for soil. However since 2021, not only sewage sludge, but also slurry, manure, and other digestate and compost producers are now facing new regulations that limit even further their use in soil (Nitrate Vulnerable Zones or NVZ) in the UK [6]. Thus to respond to the critical situation, renewed efforts are being made to reduce its disposal and promote new valorisation routes [7]. Despite the constraints with respect to tar formation and clogging [8], thermochemical conversion constitutes the most promising pathway to obtain valuable by-products from sewage sludge [9]. Unlike composting, thermochemical conversion subjects the material from moderate to high temperatures, most commonly between 300 and 700 °C [9], which has been reported to successfully kill pathogens including bacteria and viruses present in the sewage sludge [10, 11]. These treatments can significantly decompose organic pollutants, including pharmaceuticals [12, 13]. Components such as diclofenac, carbamazepine, metoprolol, and propranolol have been reported to reduce their concentrations by 39 to 97% [14]. Nonetheless, possibly the greatest advantage of thermochemical conversion is the reduction of sewage sludge volume and carbon mineralisation (greater carbon stability), which eases its management [3]. Significant attention has been given to the treatments that produce mainly syngas and bio-oil for energy recovery [15]. However, more frequently, the potential applications of the solid phase, here after referred to as char, are being investigated focusing on those treatments that obtain it as a main product [16]. This term is used to address the carbonaceous end product obtained from sewage sludge regardless of the process applied, and to differentiate it from the popular term known as biochar, which is normally obtained from biomass and that falls into at least one of the categories suggested by either of the main 3 international standards (IBI, EBC, BQM) [17–19]. Depending on the feedstock and the process conditions, the char could contain more than 50% organic carbon (C_{org}) which has increased its stability [20], enhancing its suitability of sewage sludge for soil use [21, 22]. Sludge-derived chars are specially of interest as an organic matter amendment as they increase its concentration, carbon stability and nutrients (N, P, K) in soil [22, 23], and in peat-free compost [24] reducing the mobility of heavy metals from the original feedstock [5, 25]. Given the diversity in functional units in the char surface, soil remediation has been also considered as a possible application of this residue; hence, diverse sludge-derived chars have been proven to adsorb heavy metals in contaminated soils [26] and decrease Cd, Pb, and Zn in leachate in mines [27]. The number of studies on pyrolysis and HTC performed on sewage sludge are numerous [9] but they are mainly produced separately testing diverse variables which hamper their contrast.

Common temperature ranges used for pyrochar obtained through slow pyrolysis are 300–500 °C, or as low as 200–300

°C (torrefaction), in both cases sustained from several minutes to hours. On the other hand, the hydrothermal carbonisation (HTC) process produces another type of material now mostly known as hydrochar, a solid material like pyrochar but obtained with water content as high as 80%. Hence, contrary to pyrolysis, HTC occurs in an aqueous medium normally at lower temperatures (<300 °C) and longer retention times (2–6 h) than the production of pyrochar [9]. Under these conditions, the water increases its density and its polarity changes, acquiring properties closer to those of hexane [28], being able to dissolve apolar substances, breaking organic compounds in their monomers, and thus allowing a greater number of polymerisation and acid-base reactions [29]. Due to sewage sludge containing a high percentage of moisture, an important part of the energy during pyrochar production is consumed in the drying process [30, 31]. However, HTC reduces the need of pre-drying sludge which is required for an optimal pyrolysis performance [32]. Thus, HTC opens a range of options for potential biomass sources with moisture contents [33, 34]. The choice of process results in specific structural and physicochemical properties of the carbonaceous materials [35], which are closely related to the type of feedstock [36] and potentially could bring different outcomes when added to a soil [37, 38].

Hence, if the effects of the thermochemical conversion could be better understood, the production of char could be tailored by modifying the conditions according to their use. To obtain different products, variables such as temperature and time of processing [39–41], ramping to retention times, pH adjustments, chemical doping [42, 43], or even sequential thermochemical conversions [44] and co-processing with other feedstocks [45] or coal [46] have to be taken into account. These factors will determine the physical and chemical characteristics of the pyrochar or hydrochar, and its carbon stability, and thus the best method to use it [35]. However, few studies have compared using the same source to make different types of chars making it difficult to generalise and compare results. The production and comparison of pyrochars against hydrochars obtained from the same sample of sewage sludge is yet an area that requires more evidence to assess the suitability of the technologies to produce different physicochemical characteristics.

This paper seeks to provide new information on physical and chemical attributes of hydrochar and pyrochar and their stability that could affect their behaviour once added to a matrix, such as soil, as an amendment. Two types of char obtained from pyrolysis (pyrochars) and two others obtained from HTC (hydrochars) using the same feedstock of anaerobic digested sewage sludge were compared.

We expect that (i) pyrolysis and HTC to have a significant effect on sludge properties producing different chars using the same feedstock and (ii) thermochemical conversions will

increase carbon stabilisation and porosity of sludge, best using higher temperatures of pyrolysis.

2 Materials and methods

A sample of the final thickened anaerobic-digested sewage sludge (operating temperature 35 °C) at 85 % wt moisture, SS, obtained from a municipal sewage treatment plant in Spain, was used as feedstock for the thermochemical conversions. This water treatment plant features a biological treatment that uses activated sludge process, and which mixed liquor is then passed through the ultrafiltration membrane technology to separate the sewage sludge.

2.1 Thermochemical conversions to produce pyrochars and hydrochars

Two types of pyrochars and two types of hydrochars were produced from a sample of sewage sludge (SS), at the Polytechnic University of Madrid. Settings were chosen to ensure the production of materials with significant physicochemical differences with the intention to use them afterwards in a pot study. Pyrochar samples were prepared as follows: 500 g of SS was oven-dried at 105 °C for 48 h and then placed in a metallic crucible of 1-L capacity and pyrolysed in a Heron electric furnace (model 12-PR/300 series 8B). The experiments were performed in the presence of nitrogen (40 mL/min) by increasing the temperature at a rate of 3 °C min⁻¹. The samples were pyrolysed at 300 °C for 1 h (P300-1) or 400 °C for 1 h (P400-1). The retention time of 1 h was used to perform slow pyrolysis and to compensate the lower temperature settings selected to obtain two chars aiming to increase organic matter in soil, with different degrees of carbon stability and physicochemical properties, based on previous research [47, 48].

Hydrochar samples were prepared as follows: SS that had been oven dried at 105 °C for 24 h was mixed with deionised water to obtain a controlled water content of 0.2 (g/g) (80% wt moisture). In an industrial setup, this step would be omitted, and the feedstock would be used with the original humidity as long as it is above 80% wt, instead of the adjusted one. Here for comparison, both processes used dried feedstock and water was added in HTC only. Then, the mixture was placed inside the hydrothermal reactor of 1-L capacity (Demede S.L, Spain). The experiments were performed at 180 °C and 240 °C by increasing the temperature at a rate of 3 °C min⁻¹ and then maintained for 4 h once the target temperature was achieved (hereafter referred to as H180-4 and H240-4, respectively). An intermediate retention time of 4 h was used to allow enough time for the reactions to take place and the temperatures were selected to obtain enough physicochemical

contrast without compromising production efficiency based on previous research [49]. When the process was completed the hydrochar was filtered by using a sieve and gravity. Both pyrochars and hydrochars were oven-dried at 80 °C for 24 h for transportation.

2.2 Analytical methods

All char samples were weighted, crushed, and sieved through a 2-mm mesh. The following physical-chemical analyses were carried out for all samples: moisture content and organic matter through loss on ignition (LOI) (BS EN 13039:2000) using 1 g of sample at 550 °C [50]. This technique was selected for its practicality when analysing numerous samples at once and for the low amount of sample required. To determine the content of carbonate, a further ashing was performed at temperatures >950 °C, using the same samples after measuring their weight loss at 550 °C. Contents were calculated as follows:

$$\text{Moisture (\%)} = \frac{(m_1 - m_2) \times 100}{m_1 - m_o} \quad (1)$$

$$\text{LOI(\%)} = \frac{(m_2 - m_3) \times 100}{m_2 - m_o} \quad (2)$$

$$\text{CaCO}_3(\%) = \frac{(m_3 - m_4) \times 100}{m_2 - m_o} \quad (3)$$

$$\text{Ash (\%)} = \frac{(m_4 - m_o) \times 100}{m_2 - m_o} \quad (4)$$

where m_o is the cup weight (T); m_1 is the sample plus cup measured in balance; m_2 is the total weight after drying a minimum of 17 h, in our case we did 24 h; m_3 is the sample after first ignition at 550 °C plus cup (ashes + inorganic C); and m_4 is the sample plus cup after second ashing at 950 °C (only ashes).

To compare the carbonisation degree the sludge sample, pyrochars, and hydrochars were analysed using four replicates per sample, for total C, H, and N (expressed in %) through elemental analysis. For this, each sample was oven dried at 150 °C, 24 h prior to the analysis, and 20 mg ± 0.001 mg of fine char sample (crushed to <2-mm particle size) was weighed (Oakleyweight Sartorius balance Pro 11) and placed in the Elemental Analyser (Isoprime Elementar EL III CHN).

High heating value (HHV) to compare SS, pyrochars, and hydrochars to fossil carbon was estimated by using Dulong's approximation [28]:

$$HHV \text{ (MJ/kg)} = 0.3383 \cdot C\% + 1.422 \cdot H\% - (O\%/8) \quad (5)$$

where $O\%$ is obtained as $O\% = \text{Ash}\% - C\% - N\% - H\%$ using $\text{Ash}\%$ (%) obtained after LOI at 950°C .

To quantify the effect of the different thermochemical conversions on the surface functional groups, Fourier-transform infrared spectroscopy (FTIR) contrast was performed with a Vertex 70 FTIR spectrometer, which uses Attenuated Total Reflection (ATR) to give an insight of the process efficiency and scan functional group changes after thermal processing. Each sample was ground to fine dust using a mortar. Approximately 1 g was placed on top of the crystal and analysed 10 times to obtain an average of functional groups for each sample. For each reading the data was transformed from ATR to absorbance (ABS) to transmittance (T) and then balanced to make all samples comparable using software OPUS_7.5.18 [51]. This methodology removes noise from the spectrum and places all results in the original position in the axes, making all samples comparable to one another. After correcting all curves, the means were calculated for each sample using Excel 2016.

Following, to assess the stability degree of the organic a thermogravimetric (TG) and derivative thermogravimetric (dTG) thermal analyses of the samples were conducted in a Pyris 1, Perkin Elmer; as for these analyses, 80 mg of sample was heated at $15^\circ\text{C min}^{-1}$ until 850°C under air atmosphere using a flow of 40 mL min^{-1} [47, 52].

Physical properties like specific surface area (S_{BET}), mesoporosity (10–50 nm), and microporosity (<10 nm) were determined with a Brunauer–Emmett–Teller (BET) surface area analyser 3P Meso 222 sorption analyser (3P instruments) using nitrogen as the adsorbate to assess structural changes.

2.3 Statistical analyses

The statistical analysis of experimental data was undertaken for Multivariate and Principal Component Analysis (PCA)

followed by clustering analysis using K -means and hierarchy in JMP-16. Variables studied were expected to be constant amongst individuals, fixed effects. The analysis of variance was performed through one-way ANOVA followed by a post hoc analysis. The least significant differences to compare the means were obtained with the Tukey test with a probability level of 5% ($p < 0.05$) using STATISTICA 13.3.704.19.

3 Results and discussion

3.1 Carbonisation degree of pyrochars and hydrochar

The product yield obtained varied depending on the thermochemical process and temperature selected, with a general reduction of the efficiency in dry basis at higher temperatures (H140-4: 74%, H240-4: 64%, P300-1: 78%, P400-1: 59%). The yield for HTC was in the range reported previously (45–75%) [53] but was higher than yields reported for torrefaction (20–40%) and slow pyrolysis (35–55%) [54]. These differences could be related to differences in the feedstock, on the type of reactor used, ramping, and retention time. As expected, the temperature of both treatments significantly affected the organic matter content and stabilisation of the sewage sludge sample. As can be seen in Table 1, SS had the highest OM content (68.4%). The lowest OM content was for the pyrochar obtained at 400°C (46.7%). After thermochemical conversions, OM was reduced as follows: H180-4 (16.4%), H240-4 (21.5%), P300-1 (3.5%), and P400-1 (31.7%) from SS (Table 1). Therefore, compared to other chars, the pyrochar P300-1 reduced the least concentration of labile organic matter. Moreover, as opposed to the other pyrochar P400-1 and hydrochars, P300-1 had a higher total C and N content (Table 1) than the original sludge (SS). These results were similar to those reported by Figueiredo et al. [55]. For all thermochemical conversions, total N

Table 1 Main properties of sewage sludges (SS), pyrochar from pyrolysis, and hydrochar from hydrothermal carbonisation of SS

Sample	Moisture content (%)	LOI (%)	CaCO_3 (%)	Ash (%)	H:C _{org}	O:C _{org}	C:N
SS	3.5 ab	68.4 e	5.7 f	28.7 b	1.11	0.51	6.38
H180-4	2.8 ab	57.2 c	4.5 c	39.8 d	1.04	0.44	8.85
H240-4	2.8 b	53.7 b	4.1 b	42.2 e	1.08	0.35	9.50
P300-1	1.7 ab	59.2 d	6.1 d	37.7 c	0.95	0.32	6.71
P400-1	0.3 a	46.7 a	4.6 a	50.7 f	0.75	0.23	7.28

Values in column followed by the same letter are not significantly different ($p = 0.05$) using the Tukey STATGraphics Centurion for Homogeneous Groups. Moisture content (%), LOI (%), CaCO_3 (%), and Ash (%) values were obtained from dried samples

SS = sewage sludge dried 105°C , 48 h; H180-4 = hydrochar from SS at 180°C for 4 h; H240-4 = hydrochar from SS at 240°C for 4 h; P300-1 = pyrochar from SS at 300°C for 1 h; P400-1 = pyrochar from SS at 400°C for 1 h

was partially lost, perhaps volatilised, or solubilised. In a comparison study of N compound transformation during pyrolysis and HTC, Liu et al. indicated a loss of N through deamination, formation of HCN, and oxidation of NH_3 to N_2 through heat [56]. Hydrochars from sewage sludge tend to have a lower N content but a higher stability due to N transformation from ammonium inorganic salts and labile proteins to heterocyclic-N compounds. Thus, the C:N ratio increased in particular with increasing temperature (Table 1), which agrees with result findings by Barriga et al. and M. Paneque et al. [37, 57]. Soil fertility and crop productivity are expected to be greater in soils amended with char with C:N < 9 ratios [58] which would favour pyrochars over hydrochars (Table 1). The highest C:N ratio was for H240-4 (C:N = 9.5). Nevertheless, according to Sousa and Figueiredo et al. [59], at a C:N lower than 30, it is likely that the nitrate content would be available due to a balance of net N mineralisation and immobilisation.

This is the case for all our chars which could favour crop production if used as soil amendment.

After thermochemical conversions H:C and O:C ratios of SS were considerably lower in both hydrochars and pyrochars, as shown in the Van Krevelen graph (Fig. 1), favoured by higher temperatures and pyrolysis [60, 61]. Thus, the characteristics of both SS changed towards sub-bituminous coals [62]. The use of thermochemical conversions on sewage sludge is being studied for energy purposes [63]; nonetheless, in our case, *HHV* was significantly lower in H180-4 (16.44 MJ kg⁻¹) and P400-1 (14.93 MJ kg⁻¹) from 17.94 MJ kg⁻¹ in SS (Table 2) [28].

The reduction of H:C ratio suggests a further condensation and possible formation of aromatic compounds whilst a lower O:C could be related to hydrolysis and the loss of polar functional groups. The changes in bonds and functional groups in chars' surfaces were assessed through spectroscopy.

Fig. 1 Van Krevelen graph. SS = sewage sludge dried 105 °C, 48 h; H180-4 = hydrochar from SS at 180 °C for 4 h; H240-4 = hydrochar from SS at 240 °C for 4 h; P300-1 = pyrochar from SS at 300 °C for 1 h; P400-1 = pyrochar from SS at 400 °C for 1 h

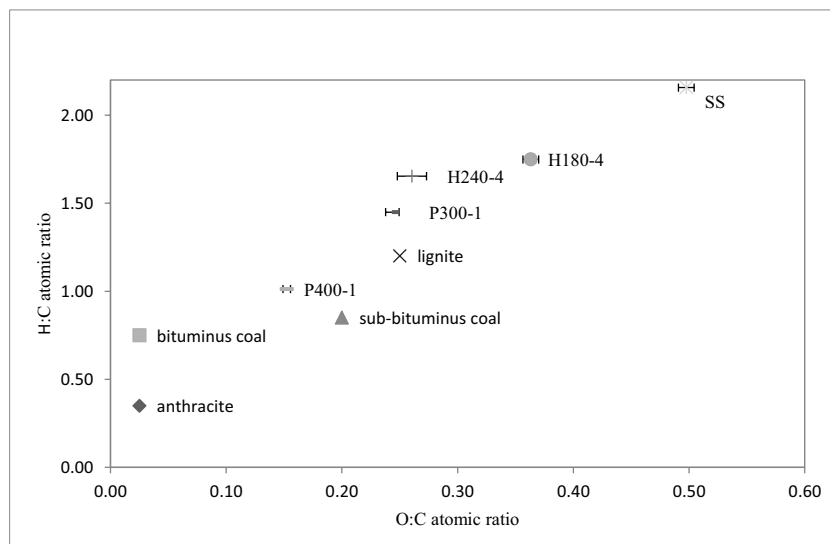


Table 2 Elemental analysis and *HHV* predicted of sewage sludge and corresponding hydrochar and pyrochar samples

Samples	Elemental analysis (%)					<i>HHV</i> predicted ² (MJ kg ⁻¹)
	C	H	N	S	O ¹	
SS	35.11 a	6.31 e	5.50 d	-	23.30 d	17.94 cd
H180-4	33.90 a	4.94 b	3.83 a	-	16.41 c	16.44 b
H240-4	34.98 a	4.82 ab	3.68 a	-	12.15 a	17.17 bc
P300-1	38.66 b	4.67 a	5.76 e	-	12.56 a	18.15 d
P400-1	34.48 a	2.91 c	4.73 c	-	7.00 b	14.93 a

Values in column followed by the same letter are not significantly different ($p = 0.05$) using the Tukey test
 SS = sewage sludge dried 105 °C, 48 h; H180-4 = hydrochar from SS at 180 °C for 4 h; H240-4 = hydrochar from SS at 240 °C for 4 h; P300-1 = pyrochar from SS at 300 °C for 1 h; P400-1 = pyrochar from SS at 400 °C for 1 h

¹Calculated by difference with ash content from Table 1

²*HHV* estimated by Dulong approximation in A. M. Smith et al.

3.1.1 Functional group characterisation through Fourier-transform infrared spectroscopy

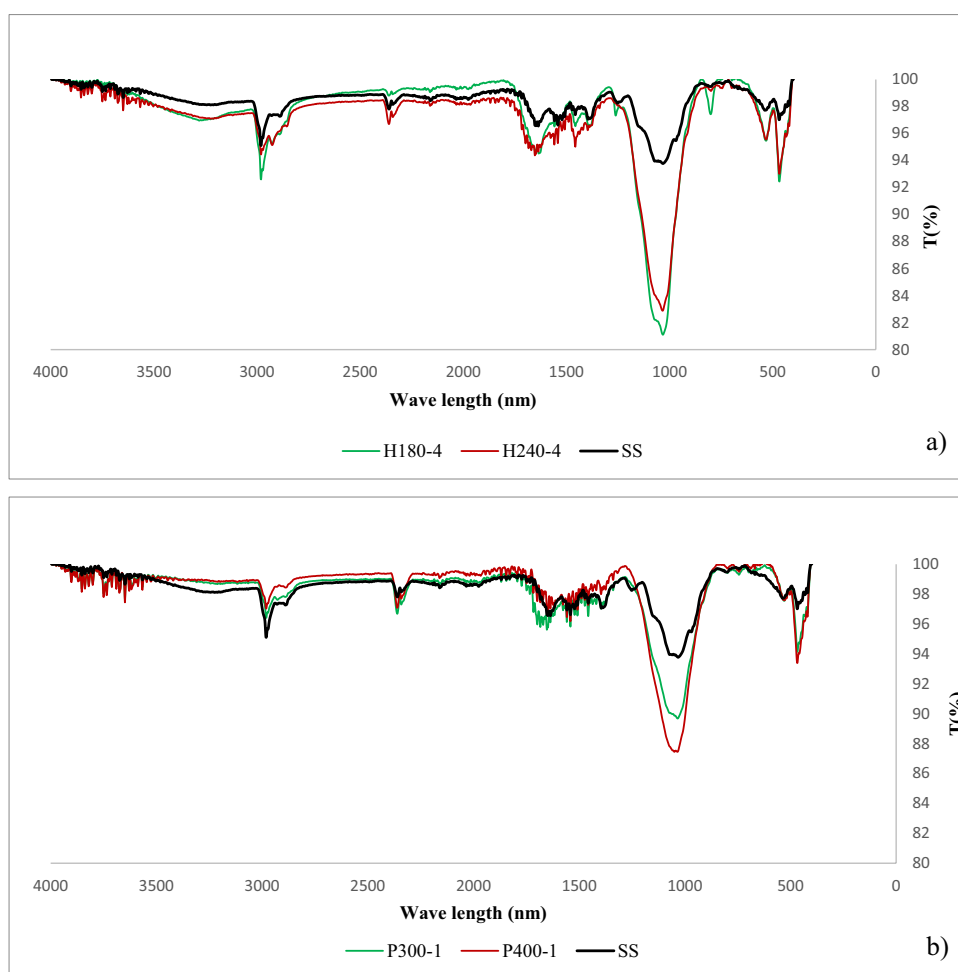
The peaks of the FTIR graph showed that no different functional groups were created after thermochemical conversions. This is commonly referred as fingerprints and agrees with previous reports for biochar derived from sludge through pyrolysis [45, 64] and HTC [63, 65]. However, although the peaks appeared in the same areas of the spectrum, indicating similar functional groups, the intensity of these peaks varied greatly depending on the area of the sample studied. Contrary to chemical analysis, this method only analyses a fraction of the surface area just like other high-precision methods, like SEM. For this reason, the average of 10 was obtained for each sample in order to compare them (Fig. 2). Thus, we suggest that FTIR analysis on similar samples should therefore be tested for homogeneity first to provide a more representative result. FTIR results of each material will be available in the supplementary information.

FTIR results show a difference in how these elements were organised on the surface area (Fig. 2). Overall, SS had peaks

for functional groups —OH (3500 cm^{-1}), —COOH ($1558\text{--}1457\text{ cm}^{-1}$), C—O (1089 and 1054 cm^{-1}), and higher aromaticity $\text{C}=\text{C}$ (1654 cm^{-1}) confirmed by less aliphatic carbons C—H (2900 cm^{-1}). According to the FTIR (Fig. 2), pyrochars showed the highest loss of functional groups and bonds from 1500 to 3445 cm^{-1} whereas hydrochars increased the peak intensity in this range. The peak from 2300 to 2400 cm^{-1} is a distinctive peak related to the CO_2 present in the air and in the sample as the reading was taken in an open surface [63].

Pyrolysis results in dehydration, followed by a decarboxylation, and, at highest temperatures, aromatisation during the carbonisation [66]. Small molecular carbohydrates are the first to decompose at $200\text{--}300\text{ }^{\circ}\text{C}$, whilst most cellulose and lignin are pyrolysed in the temperature range of $300\text{--}350\text{ }^{\circ}\text{C}$ and protein and lipid in the temperature range of $200\text{--}600\text{ }^{\circ}\text{C}$. Because of the overlapping pyrolysis temperature ranges, cross-linking reactions between different compounds could occur, which makes the pyrolysis mechanism more complex [67]. Therefore, a reduction of the signal for NH and OH bonds between 3000 and 3300 cm^{-1} , CH_3 at $2800\text{--}3000\text{ cm}^{-1}$, and CH_2 at 1431 cm^{-1} was expected with higher temperatures of

Fig. 2 FTIR. $T(\%)$ = transmittance. SS = sewage sludge dried $105\text{ }^{\circ}\text{C}$, 48 h; H180-4 = hydrochar from SS at $180\text{ }^{\circ}\text{C}$ for 4 h; H240-4 = hydrochar from SS at $240\text{ }^{\circ}\text{C}$ for 4 h; P300-1 = pyrochar from SS at $300\text{ }^{\circ}\text{C}$ for 1 h; P400-1 = pyrochar from SS at $400\text{ }^{\circ}\text{C}$ for 1 h



pyrolysis in our experiments [64] (Fig. 1). On the other hand, the solution of polymers occurs under sub-critical conditions around 200 °C followed by a re-aggregation of the monomers to form longer chains finalised by a carbonisation, where the formed polymers condense [28, 29]. Thus, having selected a hydrochar under and one above 200 °C, differences of the physical chemical characteristics between the two samples are expected. Moreover, temperature effect on hydrochars in regards of bonds proved to be greater than those between pyrochars. HTC increased asymmetric and symmetric aliphatic groups, 2964 cm^{-1} and 2848 cm^{-1} present in SS (Fig. 2), which is in agreement with results reported previously by Hossain et al. and Peng et al. [63, 64]. Both hydrochars promoted another signal assigned to aromatic C–H vibration at 2922 cm^{-1} and C = C at 1652 cm^{-1} (1730–1650 cm^{-1}). The signal C = C bond was similar for both hydrochars, but C–C was lower at 2964 cm^{-1} for H180-4 (Fig. 2). This may suggest that aromatic compounds were partially re-created by HTC but partially destroyed at higher temperatures, which was corroborated by rocking signal of aromatic C–H at 798 cm^{-1} only for H180-4. Similarly, higher temperatures of pyrolysis showed a reduction of the aromatic structures as reported by Hossain et al. [64]. P300-1 increased the signal at 1652 cm^{-1} associated to C = C but reduced it for P400-1. This aromatisation trend on sludge is in accordance with previous research.

It is important to note that all thermochemical conversions showed a stronger signal at 979–1163 cm^{-1} than SS, where H180-4 showed a higher intensity. This area is associated to SiO_2 content (1000 cm^{-1}), linked to the ash generation, and C–O bonds (950–1400 cm^{-1}). Since the materials were obtained from the same feedstock, it is likely that the C–O bonds are responsible for the differences in the peak of intensity and could suggest that these bonds were not lost but re-created through thermochemical conversions as suggested by J. Hong Zhang et al. [21]. In the case of HTC this could be due to new formed acidic groups and its derivatives which is in accordance with an increase in signal at 3200 cm^{-1} (–OH) and 1456 cm^{-1} (–COOH) for both hydrochars (Fig. 2), which is opposite to the decrease on –OH groups reported by Peng et al. [63]. Pyrochar of sewage sludge had lower presence of –OH at higher temperature as previously reported by Hossain et al. [64]. This could indicate that that –CO bonds are mainly related to new aliphatic ethers as suggested by Peng et al. and remaining acid groups from SS [63]. In the case of HTC this would indicate that these groups are promoted at lower temperatures of HTC and later destroyed at higher temperatures as the signal is lower for H240-4 than H180-4 (950–1400 cm^{-1}) (Fig. 2).

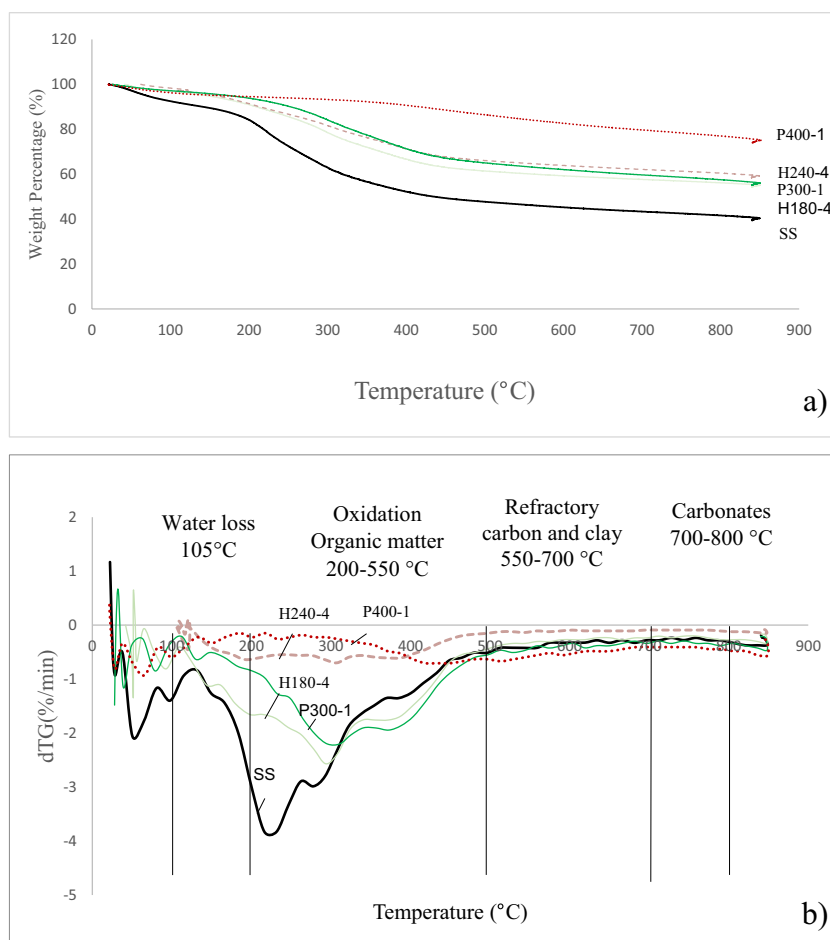
3.1.2 Carbon stability

To determine char carbon stabilisation degree, H:C_{org} and O:C_{org} molar ratios were estimated. These ratios indicated a low level of conversion for the chars when compared to those obtained from woody feedstocks [68]. Due to the presence of carbonates (Table 1), C_{org} could not be approximated to Total C but was determined by removal of OM ($\text{LOI}\%$), similarly as indicated in Bachmann et al. [50]. H:C_{org} was above 0.7 for all the samples, which is the maximum limit indicated by the International Biochar Initiative (IBI) to consider a biomass fully transformed; thus, we concluded that all treatments produced lower class biochar [69]. Even though O:C_{org} was not reduced below 0.2, which is a good indicator for biochar intended for C sequestration [68], O:C reduced to values between 0.2 and 0.4 in all chars, similarly to charcoals, indicating SS carbon stabilisation [70]. These changes in carbon stability were assessed by thermogravimetric analysis in air atmosphere of SS and the thermal derivatives. In this test, the more resistant and structurally ordered the organic fraction contained in the samples, the higher the temperature at which weight loss occurs [47]. After thermochemical conversions and in particular at higher temperatures, SS became more stable as the weight percentage curve stands above SS curve (Fig. 3; TG). Using the derivate of TG, a deeper insight can be obtained as this graph will display 4 main regions that cannot be easily spotted otherwise (Fig. 3; DTG). The weight loss from room temperature to 105 °C relates to the higher water content for the raw material (SS) than the other samples, consistent with our findings reported in Table 1. From 200 to 550 °C, when volatilisation of light compounds and the oxidation of the labile organic matter take place (Fig. 3; DTG), the sample weight was reduced further for samples produced at higher temperatures of pyrolysis and HTC. Interestingly, P300-1 showed a slightly lower reduction than H180-4 despite having a higher content of organic matter indicating a lower presence of labile organic matter (Table 1). The results presented in Fig. 3 (TG) show overall that HTC of sewage sludge obtains a similar carbon stability compared to torrefaction at the temperatures selected despite the presence of 80% wt moisture content in the reactor. These processes that run at lower temperatures are able to provide a pool of labile carbon whilst increasing the carbon stability content once present in the sludge. Nonetheless, pyrolysis at higher temperatures is preferred to achieve a higher carbon stabilisation and lower ready oxidisable organic matter (Fig. 3; dTG).

3.2 Physical structural differences

Compared to other biomass feedstocks [71], chars obtained from SS did not display large macropores; instead, a rugose surface could be appreciated in SEM analysis which

Fig. 3 Thermogravimetric analysis (TGA) (a) and derivative TGA analysis (dTG) (b). The accuracy of the TGA is ± 0.001 mg. TG's data kindly provided by Dr Ali Navabi, Cranfield's Centre for Climate and Environmental Protection, Whittle Building, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK. dTG (%/min), derivative of TG (%). $m/t = \{m_i - m(i-1)\} / \{t_i - t(i-1)\}$, where m is the mass lost (%) and t is the time (min). SS = sewage sludge dried 105 °C, 48 h; H180-4 = hydrochar from SS at 180 °C for 4 h; H240-4 = hydrochar from SS at 240 °C for 4 h; P300-1 = pyrochar from SS at 300 °C for 1 h; P400-1 = pyrochar from SS at 400 °C for 1 h



appeared to be more pronounced in chars obtained at higher temperatures (Fig. 4(a)–(e)). The quantitative differences of adsorption and structure between pyrochars and hydrochars from SS were obtained through the Brunauer, Emmett, and Teller (BET) analysis.

3.2.1 The Brunauer, Emmett, and Teller technique for porosity and surface area

Thermal derivatives used in the amendments were physically different as a result of the type of processes and temperature selected (BET; Table 3). After treating SS, larger pores were generated, and the surface area expanded. The sample of sewage sludge had low surface area 2.043 m²/g (SS) with a microporosity (<10 nm) 29% (SS). Higher temperatures generated larger pores in both processes, being P300-1 and H180-4 mainly mesoporous (10–50 nm), whilst H240-4 and P400-1 were mainly macroporous (>50 nm) (Table 3). This could be due to the gases released during the thermal processes [28, 60].

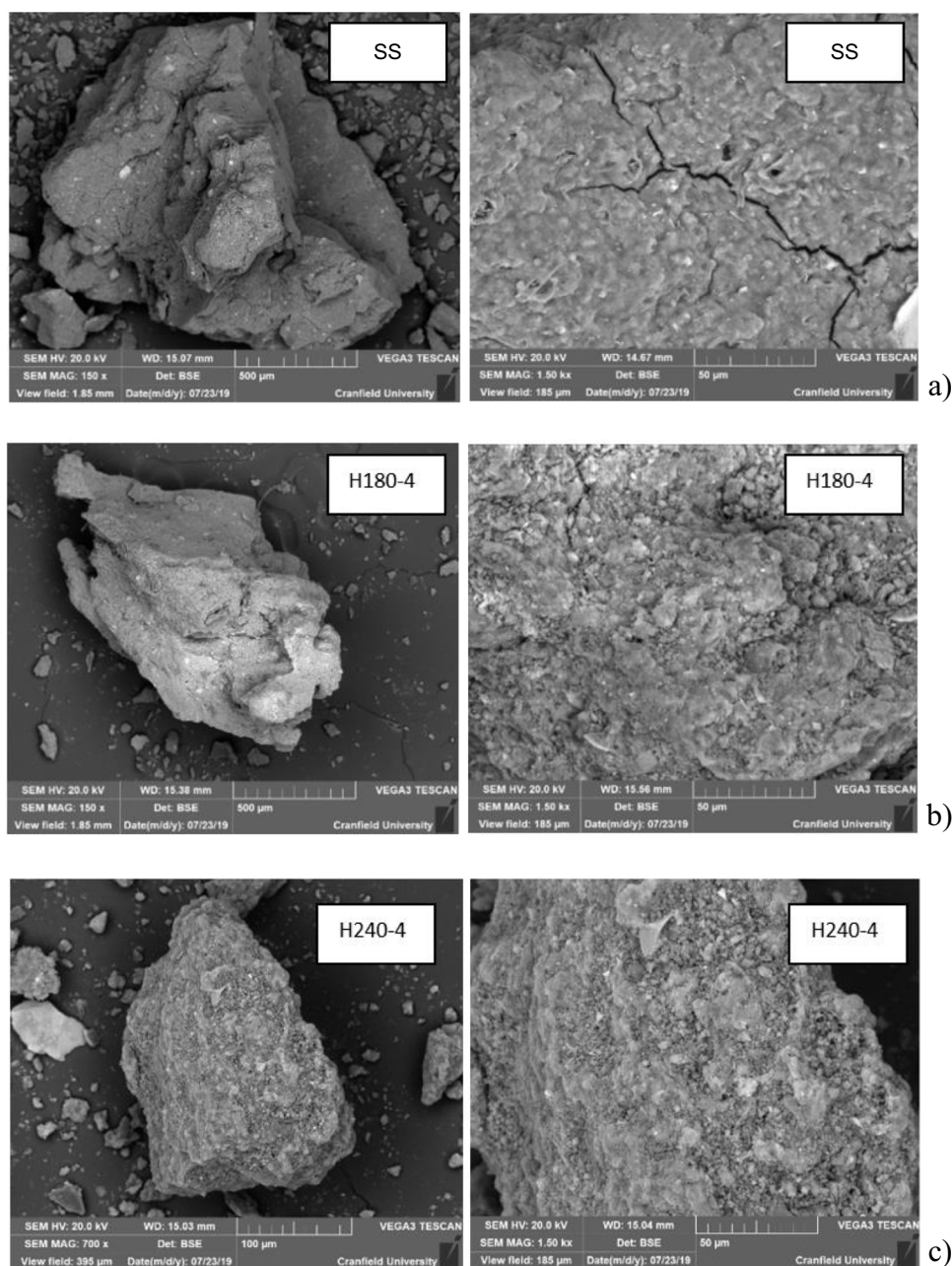
Nonetheless, the surface area of pyrochars increased from 2 m²/g SS to 4.9 m²/g for temperatures of 300 °C to 17 m²/g for temperatures of 400 °C, similarly to increases previously reported by [9], whilst HCT increased it 10 times from 2.0

m²/g (SS) to similar values independently of the temperature. Given that the materials were not subjected to an activation process, these values of surface area are considerably lower than powder activated charcoal over 900 m²/g or other activated carbons produced from sewage sludge, which have been reported to be over 500 m²/g when treated with ZnCl₂ [72, 73].

3.2.2 Adsorption isotherms of N₂ derived from the BET analysis

Given the change of porosity and surface area described above, after treating SS, the adsorption capacity towards N₂ was larger for thermal derivatives. When comparing the chars, different responses were obtained after pyrolysis and HTC, and a greater difference was obtained between pyrochars. The maximum absorbance in pyrochars 29.7 cm³/g in (P300-1) to 76.9 cm³/g (P400-1), whilst for hydrochars 108.1 cm³/g (H240-4) and 118.5 cm³/g (H180-4), indicated that hydrochars have a higher adsorption potential. This is shown in Fig. 5, through the isotherms of adsorption, which describes the equilibrium of adsorption to a surface under a constant temperature. Isotherms are considered to be of

Fig. 4 Electron-microscopic images. **a** SS = sewage sludge dried 105 °C, 48 h; **b** H180-4 = hydrochar from SS at 180 °C for 4 h; **c** H240-4 = hydrochar from SS at 240 °C for 4 h; **d** P300-1 = pyrochar from SS at 300 °C for 1 h; **e** P400-1 = pyrochar from SS at 400 °C for 1 h

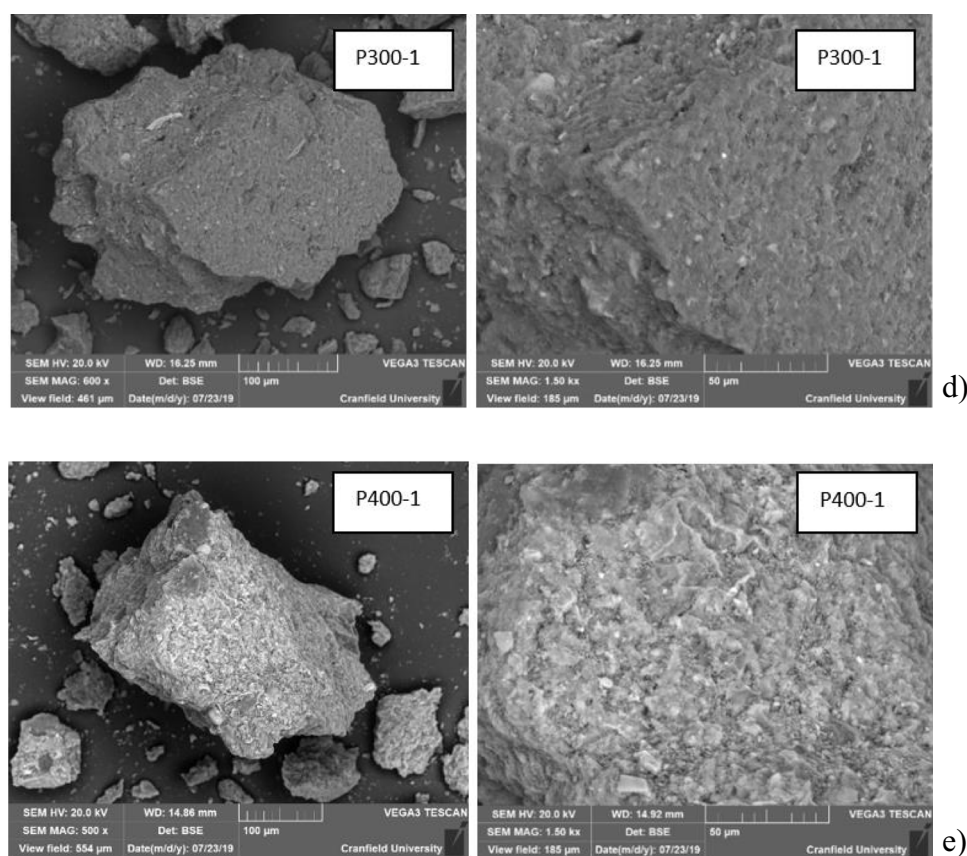


type III or IV [60, 74]. These results combined with the BET suggest that adsorption was improved with the increment of surface area and the generation of mesopores in all the samples, confirmed by the adsorption average pore with Table 3. The isotherms indicated that there was an unrestricted multilayer formation process even at higher relative pressure, as the adsorption significantly increases after relative pressure 0.75 (P/P_0) in all cases. The N_2 desorption of the samples does not behave exactly as the adsorption phase (Fig. 5). This hysteresis indicate most likely that the isotherms are of type IV, meaning that the adsorption occurs mainly on the mesoporous material, followed by a capillary condensation that takes place in these types of pores [60].

3.3 Statistical analyses

The Principal Component Analysis showed that not all the variables studied from the 5 samples correlated; only those with correlation greater than 0.3 were used. The factor matrix is listed in the supplementary information. Strong correlations (0.79) were found between *LOI*, Cation Exchange Capacity (results available in the supplementary information, and elemental analysis ratios, except C:N. The two first principal components explained the 95.2% of the total values for PC1 (84.6%) and PC2 (10.6%). Possibly the most important aspect of the statistical analysis is that, taking all analysed characteristics into account,

Fig. 4 (continued)

**Table 3** BET and mesoporous analysis (BJH) of SS and thermal derivatives (H180-4, H240-4, P300-1, and P400-1)

Sample	BET surface area (m ² /g)	Adsorption average pore width (A) (nm)	Micropore 2–10 nm (%)	Mesopore 10–20 nm (%)	Mesopore 20–50 nm (%)	Mesopore 10–50 nm (%)	Macropore >50 nm (%)
SS	2.043	24.907	35.8	11.47	6.26	17.73	46.47
H180-4	20.131	33.571	9.09	10.47	36.54	47.01	43.9
H240-4	19.998	30.896	10.41	6.95	33.86	40.81	48.78
P300-1	4.964	36.745	18.96	17.57	28.02	45.59	35.45
P400-1	16.941	25.316	11.37	11.05	30.27	41.32	47.3

SS = sewage sludge dried 105 °C, 48 h; *H180-4* = hydrochar from SS at 180 °C for 4 h; *H240-4* = hydrochar from SS at 240 °C for 4 h; *P300-1* = pyrochar from SS at 300 °C for 1 h; *P400-1* = pyrochar from SS at 400 °C for 1 h

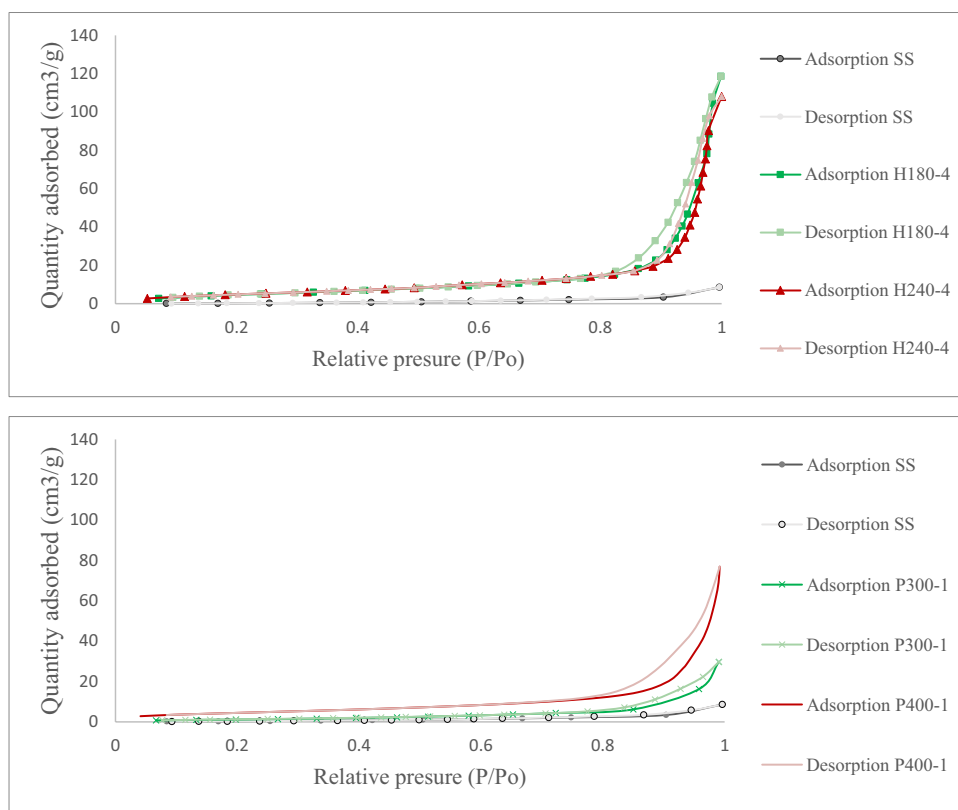
*Total pore volume filled at a relative pressure P/P_0 equal to 0.99 (A. Bsgreev, 2001)

differentiation of three main clusters (plot PC1/PC2 supplementary information: one cluster isolates the raw material (dried sludge), from the derivatives; another isolates the pyrochar obtained at higher temperature (P400-1); and the third gathers P300-1 alongside the hydrochars. The hierarchy analysis showed too that despite the differences in temperature settings, hydrochars had more similarities between them than pyrochars, and thus, lower temperatures of HTC can be selected to reduce energy consumption supplementary information.

3.4 Future research

The potential of thermochemical processes has been stated. However, several steps must be put into place in order to favour the application of such technologies at full-scale that not only concern the type of reactor and settings. Throughout the experiments it was clear the constraints and limitations the tars could produce at a larger scale, similarly to those reported by other authors [75]. Appropriate emission control systems must be put into place to achieve a cleaner process and ease its management. The installation of

Fig. 5 Pyrochar and hydrochar isotherms. SS = sewage sludge dried 105 °C, 48 h; H180-4 = hydrochar from SS at 180 °C for 4 h; H240-4 = hydrochar from SS at 240 °C for 4 h; P300-1 = pyrochar from SS at 300 °C for 1 h; P400-1 = pyrochar from SS at 400 °C for 1 h



heating bands along the pipes to reduce clogging and the use of electrostatic precipitators and cyclones in series if permitted are advised [76, 77]. Consequently, a smart design should include the recirculation of heat to reduce the input of energy for sewage sludge drying stage [78]. The optimisation of the process, both energy and economically wise, is still an area of improvement that will determine the feasibility of the technologies to firmly establish themselves in broader domains.

4 Conclusions

The number of studies on pyrolysis and HTC performed on sewage sludge has expanded over the last decade. However, the question on which technology should be applied to respond to the critical management situation remains unclear. Most research are done under different circumstances separately and using numerous variations that although provide useful information still do not allow a direct contrast. This study provides a comparison of the stability and structural properties of pyrochars and hydrochars obtained from the same sample of anaerobic-digested sludge using different temperatures. We conclude that the temperature and the type of treatment had a significant effect resulting in chars with lower labile organic matter and overall functional groups compared to the original sewage sludge

sample. Amongst the treatments selected, pyrolysis at higher temperatures achieved a greater carbon stability which can be an attractive route to store carbon in soil or another matrix (e.g., construction materials, asphalt mortar [79, 80]). In contrast, lower temperatures of pyrolysis (torrefaction) and HTC produced a material with >50% organic matter content that could be an interesting alternative to pre-treat sewage sludge to increase soil organic matter. Compared to the other samples, P300-1 was the only one that did not significantly reduce the *HHV* compared to the original feedstock (from 17.94 MJ kg⁻¹ from SS to 18.15 MJ kg⁻¹). Overall, lower temperatures of HTC obtained similar stability to the torrefied sample, which indicates that the dewatering stage could be avoided by using HTC for soil organic matter amendments and energy. Further test should be performed to assess the performance of such materials. Lastly, HTC was the preferred route to obtain a greater adsorption capacity (100 cm³/g for H180-4). The low surface area of the chars nonetheless (20 m²/g) suggested that the chars should undergo an activation process to improve their use as alternative carbon filters if desired.

Thus, the relatively low temperatures selected of slow pyrolysis and hydrothermal carbonisation could be an interesting management route for sewage sludge, generating a product with enhanced characteristics whilst contributing to circular economy.

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Data availability Data supporting this study are openly available from CORD at <https://doi.org/10.17862/cranfield.rd.24420295>.

Declarations

Ethical approval This research was conducted with approval from Cranfield University Research Ethics System.

Competing interests The authors declare no competing interests.

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