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Hydrothermal carbonization of hemp digestate: influence of operating parameters

Gianluigi Farru¹, Carla Asquer², Giovanna Cappai^{1,3}, Giorgia De Gioannis^{1,3}, Emanuela Melis², Stefano Milia³, Aldo Muntoni^{1,3}, Martina Piredda¹, Efsio A. Scano²

¹*Department of Civil-Environmental Engineering and Architecture, University of Cagliari, Via Marengo 2, 09123 Cagliari, Italy*

²*Sardegna Ricerche, VI Strada Ovest - Z.I. Macchiareddu, 09010 Uta (Ca), Italy*

³*Institute of Environmental Geology and Geoengineering, National Research Council, Cagliari, Via Marengo 2, 09123 Italy*

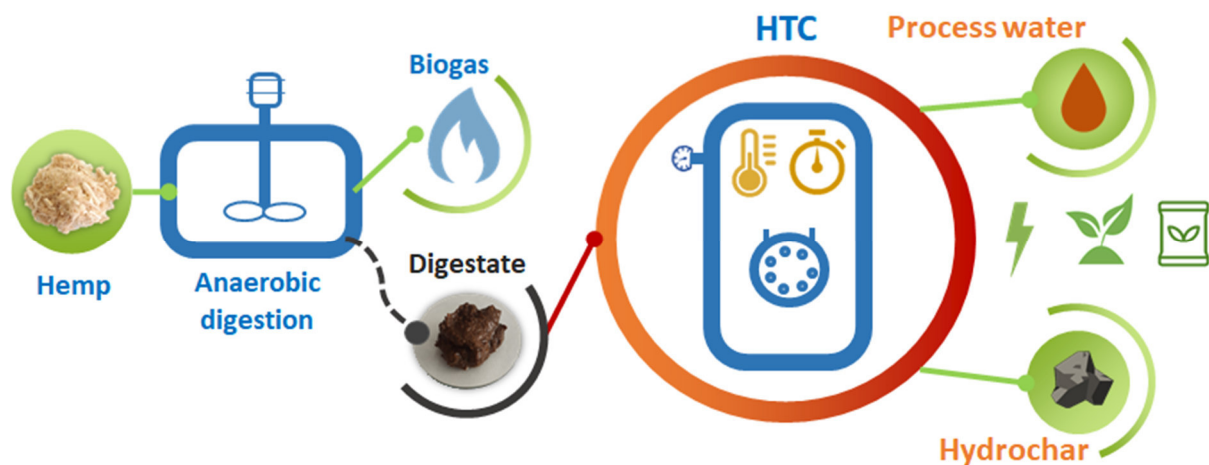
Corresponding Author: Gianluigi Farru. Email: gianluigi.farru@unica.it. Orcid number: 0000-0002-9113-0817

Abstract

In the last decade, great attention has been given to hydrothermal carbonization (HTC) as a suitable process for residual biomass valorisation, able to convert organic waste into useful materials or energy carriers. However, the involved conversion reactions that biomass components undergo are influenced by the characteristics of the treated residue along with the HTC process conditions, particularly in terms of temperature and holding time.

In this paper, the potential valorisation of hemp digestate via HTC was investigated. The study was aimed at evaluating the effect of reaction temperature and holding time on the yield and composition of produced hydrochar and on the process water characteristics. Three temperatures (180, 200, and 220 °C) were investigated along with three holding times (1, 3, and 6 h) and the obtained solid and liquid phases were characterised. Results show that the investigated operating parameters affect both the solid yield and the hydrochar and process water composition. By increasing process severity conditions through an increase in temperature and/or holding time, a drop in solid yield (89 – 60 wt%) and an increase in carbon content (+15% - +30%) and energy content (up to +22%) were achieved for the produced hydrochar compared to the feedstock, which showed suitable properties in view of its use as a fuel. Process water characteristics suggest a potential valorisation in terms of nutrient recovery or biogas production by anaerobic digestion, while the feasibility of an aerobic treatment should be carefully evaluated.

Keywords: HTC, Anaerobic digestion, Waste valorization, Hydrochar, Process water



Statements and Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Author contributions

Conceptualization: Gianluigi Farru, Carla Asquer, Giovanna Cappai; Methodology: Gianluigi Farru, Giovanna Cappai, Giorgia De Gioannis, Stefano Milia, Martina Piredda, Aldo Muntoni; Formal analysis and investigation: Gianluigi Farru, Emanuela Melis, Stefano Milia, Martina Piredda; Writing - original draft preparation: Gianluigi Farru, Giovanna Cappai; Writing - review and editing: Gianluigi Farru, Carla Asquer, Giovanna Cappai, Giorgia De Gioannis, Emanuela Melis, Stefano Milia, Aldo Muntoni, Martina Piredda, Efsio A. Scano; Resources: Carla Asquer, Giovanna Cappai, Efsio A. Scano; Supervision: Carla Asquer, Giovanna Cappai, Aldo Muntoni, Efsio A. Scano.

Introduction

The current depletion of fossil fuels is increasing the importance of biomass as a source for both biofuels or raw materials to be used in manufacturing processes. To fully exploit the potential of biomass as resource, a biorefinery concept needs to be applied, integrating different valorization processes aimed at providing multiple products, with a greater recovery yield, and hence an overall increased efficiency [1, 2]. A possible strategy

towards the sustainable production of bioenergy and bioproducts is the integration of biological processes with thermochemical conversion methods [3].

Among bio-technologies, anaerobic digestion (AD) is known as a simple and robust valorization process aimed at biogas production from several categories of organic waste. The residual non-degraded fraction is converted into digestate, typically used as soil fertilizer, whose increasing production, as well as some environmental concerns related to land application, are rising interest in alternative valorization technologies [4–7].

Hydrothermal carbonization (HTC) is a wet thermochemical process that takes place at relatively low temperatures (generally in the range 180 – 250 °C) and residence times (up to several hours) under autogenous pressure, using subcritical water to convert biomass into highly dense carbonaceous materials. HTC is particularly suitable for biomass valorization since it can be applied on high moisture feedstocks without any dewatering or drying pre-treatment. In addition, due to the high process temperature, complete disinfection from pathogens is ensured [8–10]. Within a biorefinery approach, HTC represents a very attractive option since any biomass can be processed, being the applied aqueous conditions particularly advantageous for organic residues with very high water content, such as digestate. Therefore, HTC is gaining interest as a viable route for digestate enhancement, and several studies indicate it can be applied to convert digestate into exploitable materials and sustainable energy sources, capable of adding value to the AD process [3, 11]. The two main by-products of the process are a peat-like carbonaceous solid (hydrochar, HC) and a liquid fraction (process water, PW) enriched by the most soluble compounds formed during the involved reactions. The solid hydrochar properties allow to consider it as biofuel [4, 10, 12–16], soil amender [14, 16–19], adsorbent for pollutant removal [20, 21] and the production of nanostructured materials [22, 23]. At the same time, the high presence of organics and nutrients in process water suggests the opportunity to recycle it back into AD allowing for additional energy recovery through biogas production [24, 25] or applying nutrient recovery/fertigation [11]. Nutrient recovery, such as phosphorus, has been investigated by several studies demonstrating the feasible valorization of PW from sewage sludge digestate [26–28] and agro-industrial digestate [29] for industrial-scale application. As valuable alternative option, PW may be recirculated into the HTC reactor to increase the overall process energy performance [30, 31] and the solid recovery [31], and contribute to reduce the environmental impacts [32] by reducing the use of clean water for the adjustment of the moisture content and the amount of HTC effluent.

The final quality of the produced solid and liquid by-products is significantly influenced by both the initial characteristics of the feedstock and the adopted operating conditions [10]. According to the type of feedstock, organic carbon will be differently speciated and could be differently affected by the thermochemical degradation reactions, whose extent will also be influenced by the severity of the process, especially in terms of temperature and residence time [9]. Generally, an increase in reaction severity leads to a higher release of volatile compounds and ashes, resulting in a lower solid yield and higher carbon densification in the produced hydrochar [10, 33, 34]. However, literature reports cases with the opposite phenomenon, which might be due to the recondensation of molecules that increase the solid mass product and the formation of a so-called secondary char [35–37], or to the precipitation of inorganics with the consequent increase in ash [34], especially when higher temperature or longer holding time are applied. Smith et al. [34] reported lower ash content in hydrochars from lignocellulosic materials working at 200 and 250 °C, while ash content increased with temperature for hydrochars from AD sludges. Lucian et al. [37] reported decreasing solid yield by increasing the process severity (i.e., temperature and holding time); the reversed phenomenon occurred with temperature over 250 °C (260 -280 °C). In general,

HTC temperature is known to boost dehydration and decarboxylation reactions that reduce the H/C and O/C ratios, whose extent seems more marked for longer residence times [12, 38].

Several studies have been published on the coupling of AD and thermochemical processes, like HTC, in order to boost the potential energy and material recovery from organic waste. Digestates deriving from different feedstocks (e.g., organic fraction of municipal solid waste and food waste [39–41], manure [14, 19, 42], sewage sludge [12, 43, 44]) have been investigated; Despite the studies conducted on agricultural digestates [4, 6, 45], to the best of our knowledge, digestate deriving from hemp straws has never been mentioned or studied. In the view of industrial application, deeper investigation is needed as well as a better understanding of the process path and outcomes.

In this work, the possibility to convert digestate from the AD of hemp into valuable products was studied. *Cannabis sativa* L., commonly named hemp, is a crop applied in several agro-industrial sectors (e.g., construction, food/animal feed, paper, textile), characterised by a high biomass production and root elongation, which in turn allow for a CO₂ capture capacity of about 2.5 t CO₂/ha and the protection of soils from erosion while requiring low inputs in terms of fertiliser or pesticides [46, 47]. The manifold use of hemp as well as the European and Italian regulations and incentives promoting in the last two decades hemp industry, has boosted hemp cultivation, entailing the need to properly manage the produced hemp straw residues.

Within the scope of a broader study on hemp cultivation and utilization [48], experimental tests were conducted in which the residual hemp straw was employed to produce biogas through anaerobic digestion. In this study, the obtained digestate was used as feedstock for an HTC process aimed at achieving further biomass valorisation, by producing hydrochar to be potentially used as solid fuel and process water to be eventually considered for energy recovery through biogas production or for nutrient recovery. HTC experimental tests were carried out at different temperatures (180, 200, and 220 °C) and durations (1, 3, and 6 h) to assess the influence of the adopted operating conditions on the solid and liquid by-products, that was evaluated on the basis of mass yields, composition and energy content of the produced hydrochar and composition and biogas production potential of the resulting process water.

Materials and Methods

The anaerobic digestion tests were conducted in a pilot plant having a reactor with a working volume of 0.96 m³. The reactor was mixed and heated at the temperature of 39.0 ± 0.5 °C. Seven samples of digestate were collected over a period of one year in order to compose a representative portion of the produced substrate. Throughout the tests duration, different operational conditions were adopted [48]. However, in the time of the considered digestate samples, the hydraulic retention time (HRT) was maintained within a range of 25 ÷ 48 days, and the feeding mixture was composed of hemp straw and recirculated digestate with a ratio ranging from 3.4 to 4.8 wt/wt. The total (TS) and volatile (VS) solids content in the feeding mixture were 14.3 (±1.1) wt% and 70.3 (±0.9) wt%, respectively. The TS and VS values in the digestate were 12.3 (±1.1) wt% and 67.9 (±0.8) wt%, respectively.

Digestate was hydrothermally treated at temperatures of 180, 200 °C and a holding time of 1, 3, and 6 hours. For each couple of conditions, triplicate tests were carried out to assure replicability. Moreover, three runs at 220 °C for 1h were carried out to better investigate the effect of temperature. Hydrothermal carbonization was performed in a 1.5 L pressurised reactor (Berghof, BR-1000) equipped with an electric jacket for temperature

control, a stirred shaft, and a data logging unit (Berghof, BTC-3000). For each run, the reactor was filled with around 1 L of digestate without any pre-treatment. The gas produced during the process was evacuated from the reactor and collected in gas bags for characterisation.

For the sake of comparison, HTC tests were also conducted on a representative sample of hemp straw before the digestion treatment. In this case, distilled water was added to achieve 13 wt% of solid content in the 1 L hemp mixture, which was treated at 180, 200, and 220 °C keeping the holding time constant at 1 h.

The carbonized sludge was separated through a filter press into its solid and liquid phases, namely hydrochar and process water (Figure 1). The latter was filtered at 0.45 µm and stored in plastic bottles at 4 °C for subsequent analyses, while hydrochar was oven-dried at 105 °C to evaluate the moisture content and stored in plastic bags for further characterisation. In each step, the amount of liquid and solid was estimated to evaluate the phases' repartition and obtain a final mass balance. Each sample was named with a code representing the feedstock (the initial letter), the temperature and the holding time, separated by underscores. For instance, a sample of digestate treated at 200 °C for 3 hours is referred to as D_200_3, while a sample of hemp processed at 180 °C for 1 h is named H_180_1.

Hydrochars were characterised in terms of elemental composition (C, H, N, S, O and ash content). Carbon, hydrogen, and nitrogen were evaluated through a CHNS analyser (LECO, TRUSpec) in accordance with ASTM D5373-16, while ashes were measured through a thermogravimetric analyser (LECO, TGA701) according to ASTM D7582-15. Higher heating values (HHV) were measured with a calorimetric bomb (LECO, AC500), and calculations for obtaining the oxygen content were made following EN 14918:2009.

Composite samples of process water obtained from triplicates test were characterised in terms of pH, electrical conductivity (EC), total organic carbon (TOC) through TOC analyser (Shimadzu, TOC-VCSH), chemical oxygen demand (COD), anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) via ionic chromatography (Dionex, ICS-90), macronutrients concentration (P, K, Ca) through ICP-OES (Perkin Elmer, Optima7000), and the total phenols via spectrophotometric measurements using the Folin-Ciocalteu method. The concentration of volatile fatty acids (VFA) (acetic, propionic, butyric + iso-butyric, valeric + iso-valeric, hexanoic + iso-hexanoic, heptanoic) was determined using a gas chromatograph with flame-ionization detection (model 7890B, Agilent Technology) equipped with a capillary column (HP-FFAP, 25 m, inner diameter 0.32 mm, Agilent Technology), as reported in [49]. In addition, the acute inhibition on nitrifying bacteria caused by PW was assessed through the standard method described by Ficara and Rozzi [50]. Biochemical Methane Potential tests (BMP) have been carried out according to the standard norm (UNI1601755EIT), adopting a food-to-microorganism ratio of 0.5 gCOD/gCOD in order to prevent inhibition [51]. A blank test containing only inoculum was also carried out. No nutrient solution was added. The reactors were shaken continuously and kept at 35 °C \pm 1 °C for the entire duration of the experiment. Biogas production was measured by liquid displacement. The biogas was injected through a valve in a gas chromatograph (model 7890B, Agilent Technology) equipped with a thermal conductivity detector (TCD) and two stainless columns packed with HayeSep N (80/100 mesh) and Shincarbon ST (50/80 mesh) connected in series, as reported in [49]. The BMP test ended after 28 days, when the daily methane volume was less than 1% of the cumulative assessed methane volume.

Finally, the effect of operating variables on the final properties of the produced hydrochars was interpreted through one-way ANOVA. Tukey's HSD statistical test was applied to verify whether the hydrochar characteristics were significantly different; results are expressed with the compact letter display (CLD) method.

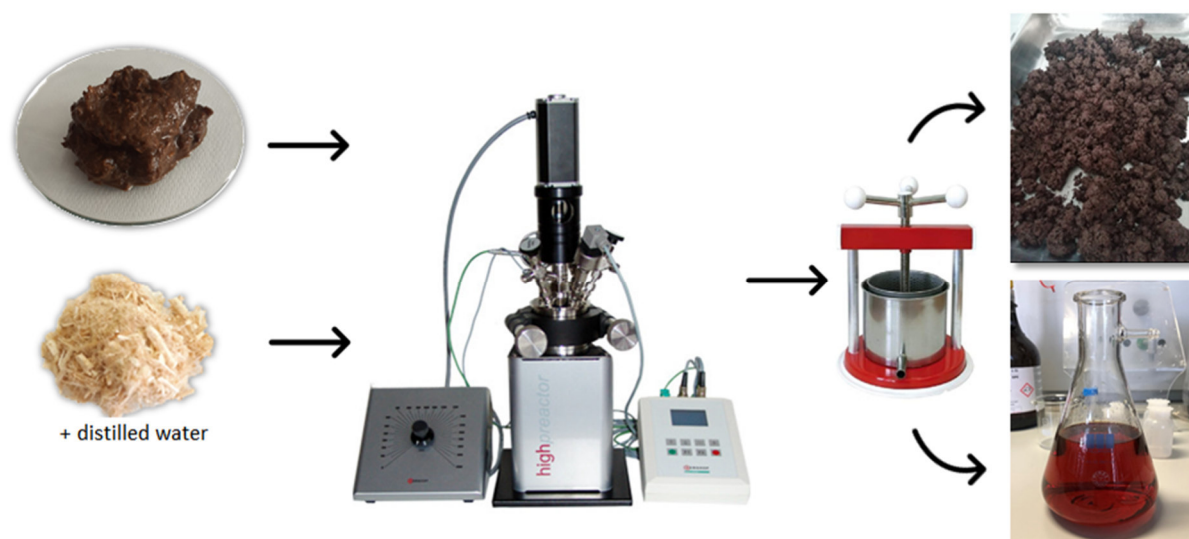


Fig. 1 Experimental setup and scheme of the operational steps

Results and Discussion

The products obtained after hydrothermal carbonization carried out at different temperatures and durations exhibited different properties. The solid yield of the hydrochars decreased with higher temperatures and longer holding time, as reported in Table 1, where statistically significant differences among the obtained hydrochar are reported. Temperature seems to be the parameter that has a higher influence on the solid yield while holding time plays a secondary role, as reported in similar studies [9, 10]. The maximum value (88.69 wt%) for digestate hydrochars was assessed at 180 °C for 1 h, while a minimum value of 72.83 wt% was measured at 220 °C for 1 h, which is consistent with results reported in literature for other types of feedstocks. Ahmed et al [12] found a decreasing solid yield treating digested sewage sludge with a 10 wt% solid input mass at 190 °C for 30 min, 1 h, 2 h, and 3 h with results of 82.4 wt%, 75.9 wt%, 71.7 wt%, and 68.3 wt%, respectively. Marin-Batista et al. [52] reports solid yield of 74.2 wt%, 67.8 wt%, and 51.8 wt%, working on sewage sludge digestate for 1 h at 180, 210, and 240 °C, respectively. These results are in line with those reported in Table 1 with a decreasing trend with higher temperature and longer holding time. Different feedstocks may have a diverse behaviour in solid yield. Mäkelä et al. [53] report values ranging between 59 wt% and 98 wt% for paper mill sludge treated at 180 and 260 °C for 1 – 6.25 h using a input solid load of 13.4 – 20.0 wt%, while Reza et al. [54] reports a solid yield of 88.5 wt% for lignocellulosic material (loblolly pine) processed at 200 °C for 5 min and lower values increasing the temperature (70.6 wt% at 230 °C and 61.0 wt% at 260 °C). A similar trend is reported for hemp hydrochars in Table 1; at 180 °C, around 80% of the input mass was recovered, while at 220 °C, the solid yield decreased to 60 wt%. The higher hydrochar yield obtained when hemp digestate was used as feedstock is consistent with the transformation occurring on hemp during anaerobic digestion. Hemp digestate is a by-product of a biological treatment in which organic compounds are hydrolysed and subsequently converted into biogas, that makes the produced digestate depleted in soluble fraction and therefore less prone to further mass loss.

The composition of the produced hydrochars is shown in Table 2. In Table 3, different letters indicate a significant difference between the hydrochars at $p < 0.05$. According to the preliminary characterisation, all the parameters

considered in the produced hydrochar were significantly different from the feedstock ($p < 0.001$). The carbon content in hydrothermally-treated samples increased with respect to the feedstock, while ash and oxygen content were reduced, indicating that they were released in the liquid and gaseous phases. As for the effect of operating conditions, higher temperatures seem to produce a significant increase in carbon concentration, while no statistically significant effect can be evidenced by increasing retention time as presented by other authors on different feedstocks [55, 56]. Hydrogen and sulphur do not present statistically significant variation at the different operating conditions adopted. Ash content is significantly lower at lower temperatures and shorter holding time for digestate hydrochars. On the contrary, an increased temperature produced a lower ash content in hemp hydrochar.

Table 1 Average solid yields of the hydrochars produced via HTC of hemp digestate at different temperatures and holding time and standard deviations. Significant differences ($p < 0.05$) among tests are represented by different upper-case letter labels for digestate and lower-case letters for hemp

| Sample | Solid yield [wt%] | CLD |
|---------|----------------------|-----|
| D_180_1 | 88.69 (± 0.68) | A |
| D_180_3 | 86.87 (± 0.70) | A B |
| D_180_6 | 85.68 (± 0.64) | B |
| D_200_1 | 85.78 (± 1.43) | B |
| D_200_3 | 78.33 (± 1.05) | C |
| D_200_6 | 73.51 (± 0.85) | D |
| D_220_1 | 72.83 (± 1.08) | D |
| H_180_1 | 79.67 (± 1.56) | a |
| H_200_1 | 65.23 (± 0.57) | b |
| H_220_1 | 60.06 (± 0.65) | c |

Table 2 Average composition of hemp digestate and hemp and the produced hydrochars in terms of C, H, N, S, O and Ash. Values reported on dry basis

| Sample | C [wt%] | H [wt%] | N [wt%] | S [wt%] | O [wt%] | Ash [wt%] |
|-----------|-------------------------|------------------------|------------------------|------------------------|-------------------------|----------------------|
| Digestate | 43.76 (± 2.04) | 5.02 (± 0.20) | 1.42 (± 0.60) | 0.10 (± 0.08) | 32.66 (± 0.79) | 17.04 (± 0.95) |
| D_180_1 | 50.30 (± 0.21) | 5.13 (± 0.13) | 1.86 (± 0.17) | 0.08 (± 0.03) | 28.53 (± 1.90) | 14.10 (± 1.78) |
| D_180_3 | 51.83 (± 1.47) | 4.89 (± 0.06) | 1.57 (± 0.51) | 0.07 (± 0.04) | 27.43 (± 1.67) | 14.21 (± 0.92) |
| D_180_6 | 50.45 (± 0.33) | 4.96 (± 0.03) | 0.91 (± 0.02) | 0.08 (± 0.06) | 29.23 (± 0.07) | 14.37 (± 0.42) |

| | | | | | | |
|----------------|------------------------|------------------------|------------------------|------------------------|-------------------------|----------------------|
| D_200_1 | 52.39 | 4.75 | 1.05 | 0.08 | 26.27 | 15.47 (± 0.38) |
| | (2.63) | (± 0.33) | (± 0.09) | (± 0.04) | (± 2.80) | |
| D_200_3 | 52.83 | 4.80 | 1.15 | 0.09 | 24.70 | 16.43 (± 0.05) |
| | (± 0.42) | (± 0.07) | (± 0.05) | (± 0.03) | (± 0.56) | |
| D_200_6 | 54.14 (\pm 1.46) | 4.90 (± 0.23) | 1.15 (± 0.02) | 0.08 (± 0.01) | 21.89 (± 2.00) | 17.84 (± 0.38) |
| | | | | | | |
| D_220_1 | 57.08 | 4.92 | 2.11 | 0.08 | 19.99 | 15.82 (± 0.06) |
| | (± 0.56) | (± 0.10) | (± 0.07) | (± 0.02) | (± 0.50) | |
| Hemp | 43.59 | 6.02 | 1.50 | 0.30 | 44.67 | 3.92 (± 2.30) |
| | (± 0.29) | (± 0.09) | (± 0.04) | (± 0.08) | (± 2.30) | |
| H_180_1 | 53.41 | 5.56 | 0.27 | 0.20 | 37.21 | 3.34 (± 1.11) |
| | (± 1.20) | (± 0.04) | (± 0.05) | (± 0.03) | (± 0.04) | |
| H_200_1 | 56.58 | 5.77 | 0.53 | 0.21 | 34.48 | 0.53 (± 3.52) |
| | (± 3.26) | (± 0.23) | (± 0.20) | (± 0.05) | (± 0.68) | |
| H_220_1 | 59.38 | 5.83 | 0.66 | 0.20 | 32.28 | 0.66 (± 0.42) |
| | (± 0.40) | (± 0.04) | (± 0.01) | (± 0.04) | (± 0.42) | |

The higher heating values measured for the different hydrochars are shown in Figures 2a-b (digestate and hemp, respectively). All the hydrochars reveal much higher HHV than the two feedstocks, with an increase between 15.6 and 22.2% in the case of digestate and between 16.5 and 26.0% in the case of hemp. An increase in temperature and/or holding time seem to produce a slight increase in HHV, as showed by other authors [43, 55]. However, no statistically significant variation was seen for digestate hydrochar (Figure 2a). Literature reports heat content for several solid materials between 5 and 39 MJ/kg. In particular, traditional solid fuels range from 15 to 33 MJ/kg for coals and coke, 7 to 19 MJ/kg for wood, 5 to 21 MJ/kg for biomass residues (i.e., seeds, pine needles, shells, grass, etc.), and 16 to 20 MJ/kg for biomass for energy purpose (i.e., wood and energy crops) [57].

The carbonization grade was assessed through the Van Krevelen diagram (Figure 3a-b), which highlights the changes caused by the combined effect of dehydration and decarboxylation reactions. Compared to the feedstocks, all the samples show a reduction of both the atomic ratios H/C and O/C, which place them in the typical areas of peat and lignite. The major shifting was obtained on x-axis suggesting a higher effect due to decarboxylation than dehydration as reported by Mumme et al. [58]. The results, along with the ash reduction and the increase of HHV, suggest that HC may be used as solid fuel for energy recovery. Other authors [13, 55, 59, 60] proposed HC from different feedstocks as potential solid fuel due to these characteristics. In particular, the reduction of ash content means less residues after combustion; however, a deeper investigation on the ash melting behaviour is needed. Moreover, the reduction of O/C reported in the Van Krevelen diagram may indicate reduced emissions during combustion. These properties are particularly advantageous when HC is applied for energy recovery.

Table 3 Tukey's HSD test results on hydrochars from digestate and hemp. Tests connected by the same letters are not significantly different

| | C | H | N | S | O | Ash |
|---------|-----|---|-----|---|-----|-------|
| D_180_1 | A | A | A | A | A | A |
| D_180_3 | A B | A | A B | A | A | A B |
| D_180_6 | A | A | C | A | A | A B |
| D_200_1 | A B | A | B C | A | A B | A B |
| D_200_3 | A B | A | B C | A | A B | B C |
| D_200_6 | B C | A | B C | A | B C | C |
| D_220_1 | C | A | A | A | C | A B C |
| H_180_1 | a | a | a | a | a | a |
| H_200_1 | b | a | a b | a | b | a b |
| H_220_1 | c | a | b | a | c | b |

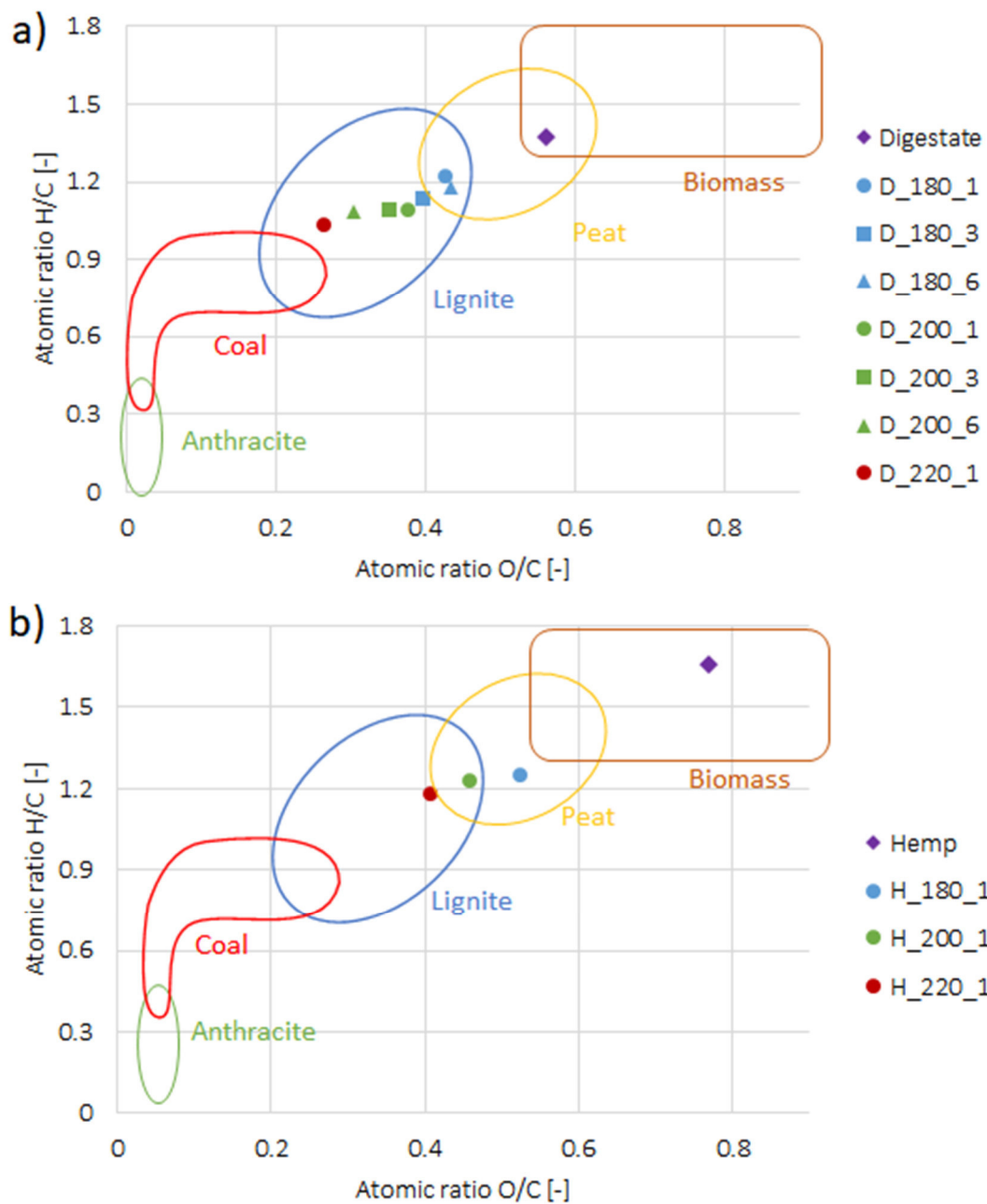


Fig. 2 Average higher heating values of the samples of a) digestate and hydrochars and b) hemp and its hydrochars

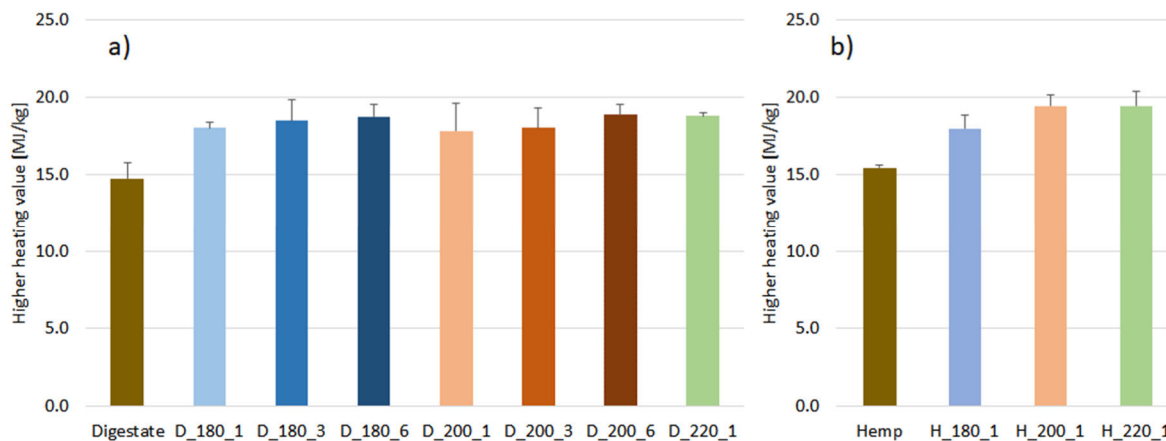


Fig. 3 Van Krevelen diagram for a) digestate and related hydrochars and b) hemp and its hydrochars

Table 4 reports the characterisation of the process water samples. Hydrothermal treatment promoted acidification in the liquid phase, in which longer holding times seem to produce a larger pH reduction, while the increase of temperature does not show a clear effect, as result by comparing PW samples from digestate treated at the same duration and different temperatures. For instance, during 1 h test on digestate, the higher pH of PW was reported for 200 °C, followed by 180 and 220 °C. Likewise, samples treated for 3 h reported the higher pH at the higher temperature, while at 6 h the behaviour seems to be the opposite. This fact may suggest that different reaction paths are followed for the diverse conditions. Under hydrothermal conditions, the degradation of different vegetative components (cellulose, hemicellulose, lignin) needs determined temperature to begin. In particular, while hemicellulose is readily hydrolyzed at 180 °C and significantly at 200 °C, lignin and cellulose need higher temperature (above 200 °C) to degrade [9, 10, 55]. The degradation of these components produces several intermediates (e.g., organic acids [9, 10]) which are partially dissolved in PW affecting its characteristics, such as pH. A different trend can be seen for samples from hemp, where the pH slightly decreases with higher temperatures. The pH of the digestate used as a feedstock was 8.50 (± 0.25), while the pH of the produced process water ranged between 7.90 and 6.78. The initial pH of the hemp used as HTC feedstock was 5.33 (± 0.12), and it dropped to acidic pH values ranging between 3.69 and 3.53 after HTC. The higher drop in pH for hemp compared to the PW from digestate may be due to the buffering effect of digestate which promote a neutralization of the acids formed during the HTC process [61]. No particular trend was found for EC in the digestate hydrochar with values around 25 mS/cm compared with the initial EC of digestate of 20.43 (± 0.03) mS/cm. In contrast, much lower values are reported for hemp hydrochars ranging from 9.03 to 8.33 mS/cm, starting from an initial value of hemp of as much as 4.23 mS/cm. For both digestate and hemp samples, TOC and COD decreased in the liquid phase as the severity of the process increased; this is consistent with the intrinsic characteristics of the HTC, based on a series of reactions generally promoted by an increase in process temperature and duration. After an initial step based on hydrolysis, with the dissolution of the solid into the liquid, there is a phase in which the dissolved carbon particles recondense in the solid portion, increasing the final carbon content in the solid phase and the nutrients content in the liquid phase [10, 61].

Table 4 Process water characterisation

| Sample | pH | EC [mS/cm] | TOC [g/L] | COD [g/L] | Cl ⁻ [mg/L] | N-NO ₃ ⁻ [mg/L] | SO ₄ ⁻ [mg/L] | P [mg/L] | K [mg/L] | Ca [mg/L] | Total phenols [mg/L] | Total VFA [g/L] |
|---------|------|------------|--------------|--------------|------------------------|---------------------------------------|-------------------------------------|----------|----------|-----------|----------------------|-----------------|
| D_180_1 | 7.62 | 26.35 | 9.36 (0.06) | 24.21 (0.76) | 2970.71 | 4.88 | - | 32.4 | 5741.0 | 194.7 | 1565.3 | 3.86 |
| D_180_3 | 7.55 | 26.82 | 9.24 (0.07) | 23.71 (0.57) | 5206.68 | 50.87 | 172.37 | 42.6 | 6474.0 | 244.1 | 1435.4 | 3.16 |
| D_180_6 | 7.42 | 27.23 | 8.99 (0.11) | 23.13 (0.35) | 4374.97 | 47.61 | 174.88 | 36.1 | 6259.0 | 173.9 | 1445.4 | 1.42 |
| D_200_1 | 7.91 | 26.50 | 6.95 (0.08) | 19.24 (0.76) | 4342.33 | - | - | 17.4 | 4759.0 | 54.8 | 1825.0 | 3.93 |
| D_200_3 | 7.81 | 26.69 | 7.89 (0.02) | 21.06 (0.29) | 4756.48 | 53.04 | 325.11 | 19.3 | 5718.0 | 212.5 | 1835.0 | 2.59 |
| D_200_6 | 7.38 | 27.93 | 7.15 (0.03) | 19.90 (0.70) | 4769.17 | 40.44 | 178.53 | 9.6 | 6920.0 | 415.0 | 1405.4 | 3.25 |
| D_220_1 | 7.34 | 28.67 | 8.80 (0.13) | 23.38 (0.70) | 3970.50 | - | 171.34 | 33.4 | 6688.8 | 409.6 | 2014.8 | 3.83 |
| H_180_1 | 3.69 | 9.03 | 12.31 (0.18) | 29.85 (0.50) | 1029.95 | 137.93 | 44.69 | 33.2 | 1768.0 | 351.5 | 1476.0 | 8.60 |
| H_200_1 | 3.55 | 8.95 | 11.31 (0.13) | 27.11 (0.35) | 962.74 | 115.06 | 46.25 | 40.6 | 1805.0 | 323.1 | 1907.6 | 5.07 |
| H_220_1 | 3.53 | 8.33 | 9.32 (0.08) | 23.05 (0.76) | 1048.68 | 133.92 | 31.23 | 16.5 | 1599.0 | 397.1 | 2083.4 | 3.17 |

Figure 4a-b show the values of the inhibiting concentration for the different PW samples produced from hemp digestate and hemp at the different process conditions. At constant temperature, toxicity increases as the residence time increases (from 1 to 3 h) and then decreases to 6 h. The lowest toxicity stands out in the case of the D_180_6; therefore, lower temperature and higher holding time seem to result in a lower formation of toxic compounds. With a constant holding time of 1 h, the toxicity decreases with increasing process temperature (from 180 to 200 °C) and then increases to 220 °C for digestate; in contrast, for hemp samples, the higher the temperature, the higher the inhibition. There are no significant differences between the process waters from H_180_1 and H_200_1, while the sample produced at 220 °C shows more significant toxicity. The high acute toxicity presented by all the PWs suggests that the treatment in traditional wastewater treatment plants where a nitrification stage is present it may be not a feasible option. However, it may still be a valuable alternative after an acclimation phase. The chronical effects of PW on nitrifying bacteria should be carefully evaluated. Nevertheless, it is an interesting preliminary result which may be used as indicator for the presence of toxic substances as demonstrated in a recent previous work in Farru et al. [19] where the bioassay was used to predict the phytotoxicity of PW on the germination of cress seeds.

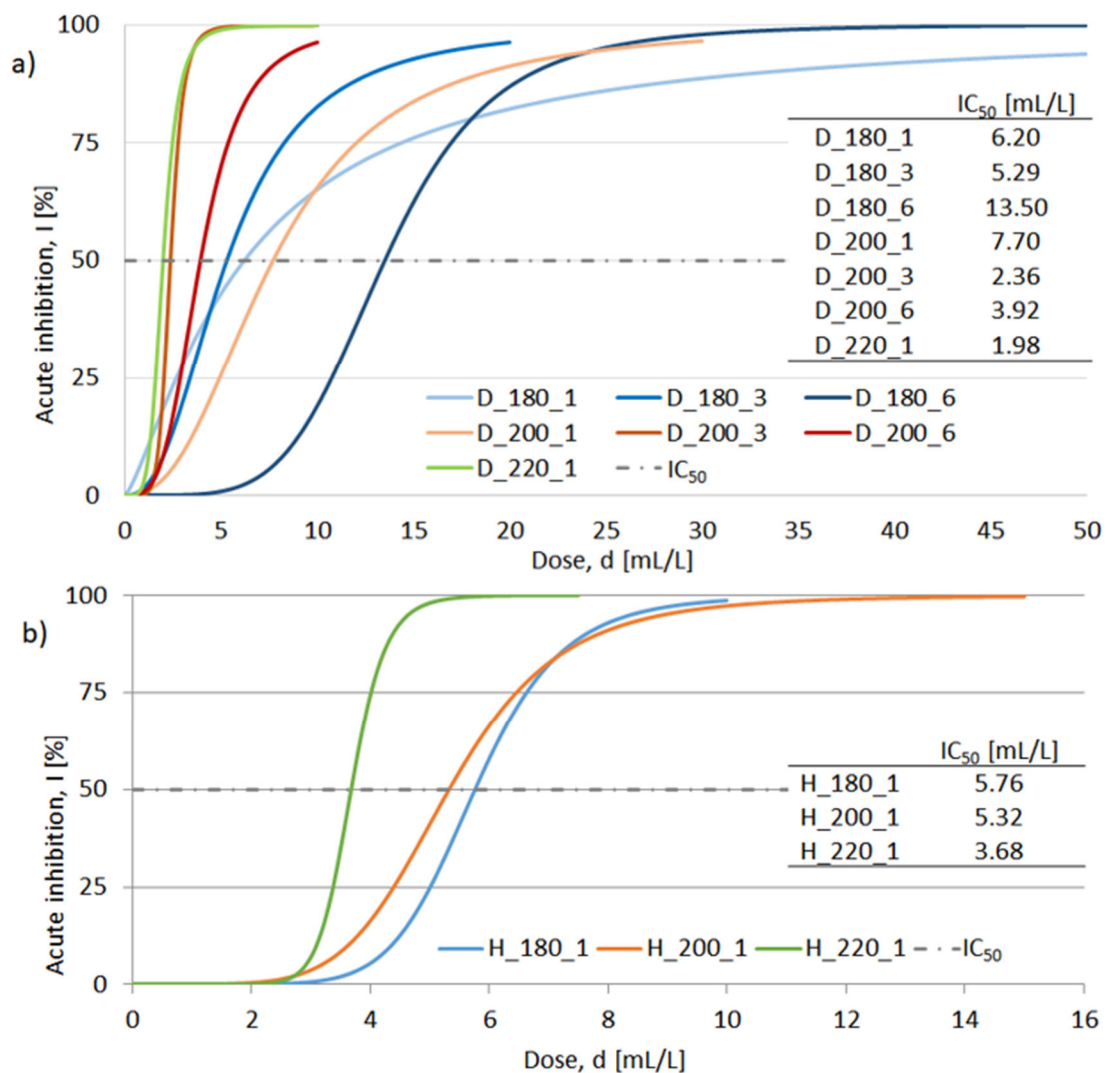


Fig. 4 Dose-inhibition curves of the toxicity test on process water derived from a) digestate and b) hemp

The organic content in process waters, particularly in terms of volatile fatty acids (VFA, Table 4), suggests their potential valorisation in anaerobic digestion processes to produce biogas. Lower TOC and COD concentrations were found in process water from hemp digestate treatment, which is consistent with the assessed higher solid yield. The macronutrients (P, K, Ca) content in process water, resulting from the dissolution of the solid material in the produced liquid phase, may suggest the use of PW in fertigation or their recovery for the production of fertilisers as proposed by other authors [29, 62, 63]. However, process water contains high concentrations of phenols that may have adverse effects when PW is directly used on soil. The higher the temperature, the higher the concentration of total phenols, while a longer holding time seems to reduce the amount of these compounds.

In Figure 5, the concentration of total phenols in PW from HTC of hemp and hemp digestate is presented together with IC₅₀ values. The inhibition on nitrifying bacteria is stronger in PW from hemp when higher amounts of total phenols are present, with an increase with temperature. Total phenols may contain compounds which can have toxic effect on aerobic bacteria. However, according to the figure, different compounds could be formed in PW from hemp digestate since a diverse trend was found, especially in samples generated at 180 °C. Considering the holding time, toxicity increased at 3 h compared to 1 h and then decreased at 6 h. Regarding samples treated at 1h and different temperatures, PWs from D showed increased concentration of phenols which correspond at higher toxicity. The higher amount of total phenols and the higher inhibition was found in D_220_1 and H_220_1.

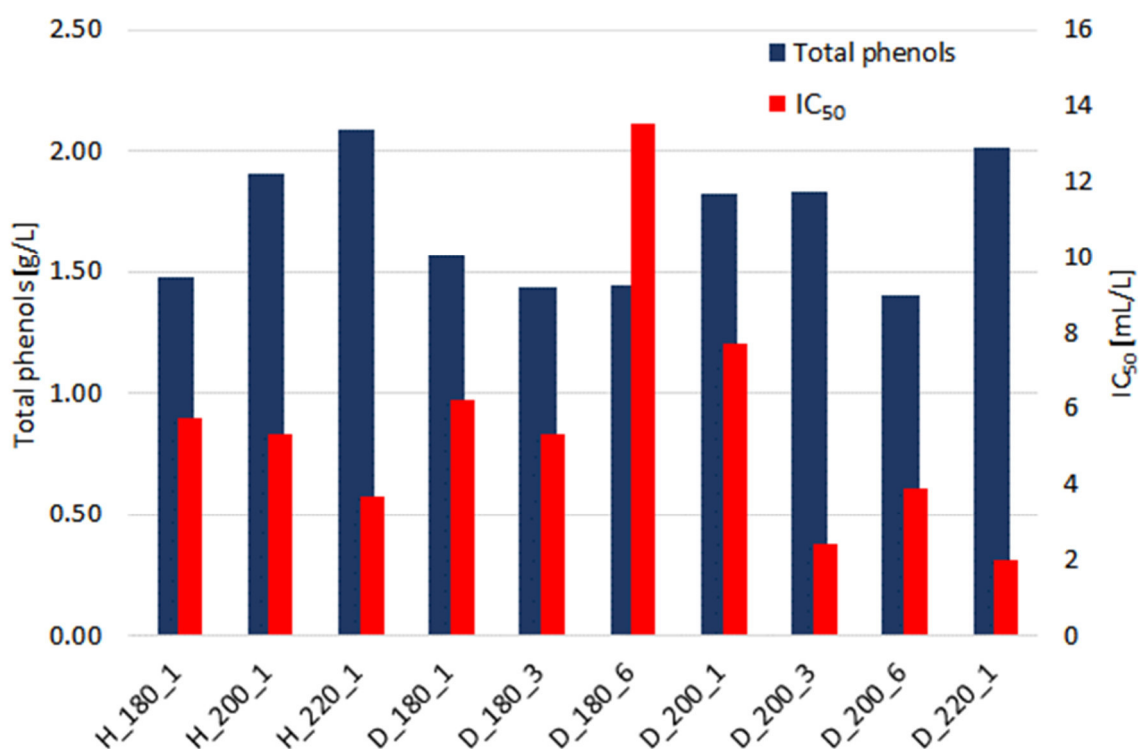


Fig. 5 Concentration of total phenols and IC₅₀ in PW samples form HTC of hemp and hemp digestate

The specific cumulative methane production yield (SMY) assessed through BMP test of the PW is shown in Figure 6a for digestate and Figure 6b for hemp. The results are provided as mL CH₄ produced per initial g COD in PW. The methane production yield was greatly affected by the HTC temperature. Specifically, when the HTC temperatures kept at 180 °C, higher SMY were obtained for both digestate and hemp, than those obtained for higher temperatures. After 28 days, SMY reached 75.8, 63.5, and 50.9 mL CH₄/g COD_i for digestate and 113.6, 82.3, and 76.3 mL CH₄/g COD_i for hemp, at 180, 200, and 220 °C, respectively. Increasing the retention time of the HTC process on digestate from 1 to 6 hours has a milder effect on the SMY, with an increase of 16% and 15% at 180 °C and 200 °C, respectively. The observed results fall within the range reported by Merzari et al. [64] and similar results were also found by Erdogan et al. [65, 66] working on HTC PW from orange peels and chicory roots. This result could be linked to the higher concentration of inhibitors, such as phenols, in the PW when increasing the HTC temperature (see Table 4), as also underlined by the aerobic inhibition curves (Figure 5). Moreover, other compounds formed during the HTC process, and not specifically identified, could have had an inhibitory effect against AD. This aspect is relevant considering that more than 50% of soluble TOC has not been identified.

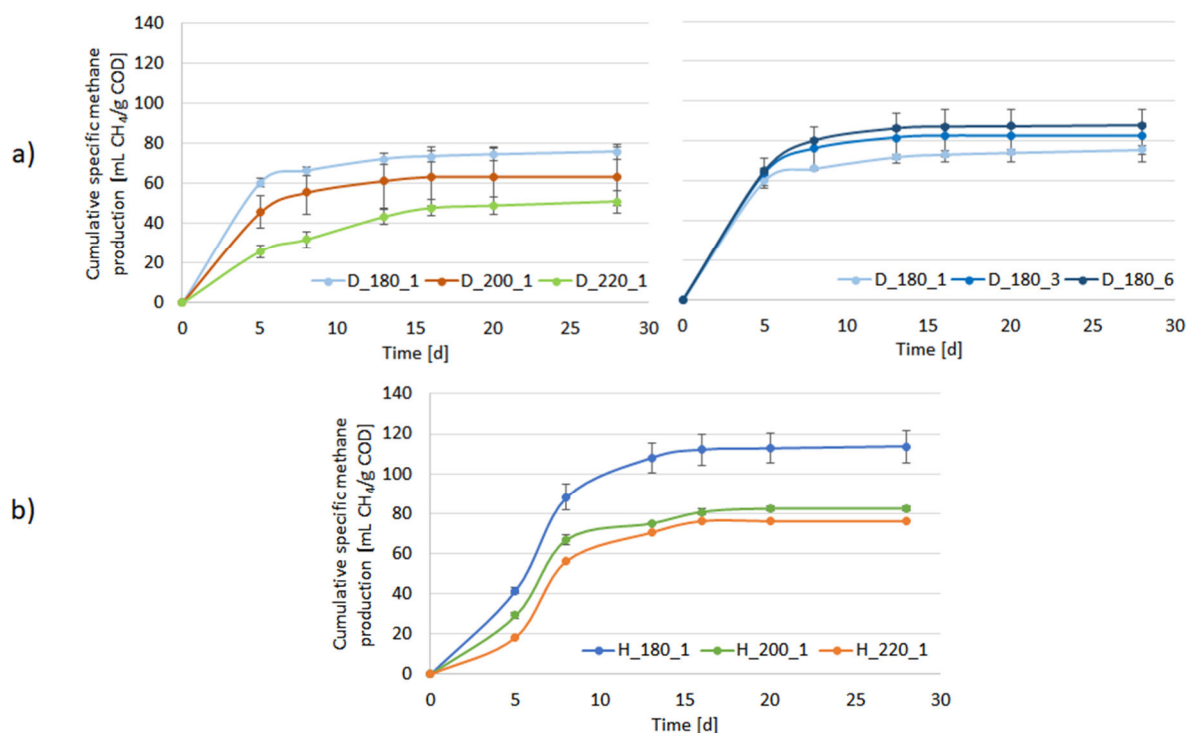


Fig.6 Cumulative specific methane production from PW deriving from hydrothermal carbonization of a) digestate and b) hemp treated at different operative conditions

Conclusion

Anaerobic digestion is a technology commonly used for the energy valorisation of residual biomass, but it produces a digestate that requires appropriate valorisation in the perspective of sustainable management. The

integration of AD with HTC has been recently proposed as an promising approach for increasing the overall recovery of energy and added value products from the hemp supply chain.

The characterisation of the hydrochars suggests that this process applied to wet feedstocks may produce added-value products. The properties of the produced hydrochar were improved compared to the input material, particularly in terms of carbon and energy content. As far as the effect of process conditions is considered, an increase of process severity with reference to higher temperatures and longer holding times resulted in a decreased solid yield and a higher carbon enrichment. Therefore, since there were no significant differences in HHV under different operating conditions, the hydrothermal conversion may be performed using lower temperatures and shorter holding time. Such operating conditions can still assure good properties in the solid products yet involving less energy consumption, that is a great advantage in view of industrial applications. In fact, the Van Krevelen diagram showed an achieved carbonization grade similar to peat or lignite, which, along with the increase in HHV, provide good perspectives for hydrochar's use as fuel. Moreover, the hydrochars characteristics, such as high pH, peat-like properties, and complete disinfection, make them potentially suitable as soil amendments. In view of industrial application, also the fate of the process water should be taken into account. According to the obtained results, process water may be valorized for nutrient recovery, while the use in irrigation in agriculture should be deeper investigated due to the presence of high amount of organic matter. The disposal of process water in a traditional wastewater treatment plant where nitrifying bacteria operates should be carefully evaluated since the PWs showed high acute inhibition. The AD of process water seems to be the most promising valorization pathway. However, a deeper analysis of carbon speciation in PW should be performed to assess the most feasible management option.

The results of this study can provide useful information on the potential integration of HTC with AD in the management of agro-industrial waste.

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