Co-hydrothermal carbonization as a potential method of utilising digested sludge and screenings from wastewater treatment plants towards energy application

Nina Kossińska [a], Anna Grosser [b], Marzena Kwapińska [c], Witold Kwapiński [d], Heba Ghazal [e], Hussam Jouhara [f,g,*], Renata Krzyżyńska [a]

[a] Wroclaw University of Science and Technology, Faculty of Environmental Engineering, Wyb. Wyspianskiego 27, 50-370, Wroclaw, Poland
[b] Institute of Environmental Engineering, Czestochowa University of Technology (CUT), Czestochowa, Poland
[c] Department of Chemical Sciences, University of Limerick, Limerick, V94 T9PX, Ireland
[d] Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland
[e] School of Pharmacy and Chemistry, Kingston University, Kingston Upon Thames KT1 2EE, UK
[f] Heat Pipe and Thermal Management Research Group, College of Engineering, Design and Physical Sciences, Brunel University London, Uxbridge, Middlesex, UB8 3PH, UK
[g] Vytautas Magnus University, Studentu Str. 11, LT-53362, Akademija, Kaunas Distr., Lithuania

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ABSTRACT

Anaerobic digestion is one of the most recommended methods for utilising sewage sludge produced by wastewater treatment plants. However, the increasing amount of micropollutants in digested sludge can significantly limit its future utilisation. Recent studies suggests that the hydrothermal carbonization process can be used as a complementary method for sludge management, due to the improved quality of solid products - hydrochar. Moreover, this allows for the possibility of reusing liquid by-products in the anaerobic digestion process for biogas production. However, hydrochar generated from hydrothermal carbonization has a higher concentration of heavy metals and low energy value, which limits its use in agriculture and energy sectors. This study highlights a partial resolution to this problem, by mixing digested sludge with screenings in the co-hydrothermal carbonization process. The findings of this study show improvements in the properties of hydrochar including total solids measured according to ISO, inorganic fractions determined by inductively coupled plasma optical emission spectrometry and higher calorific values measured by the calorimetric bomb. Biomethane potential tests were conducted on liquid by-products. The results showed an average increase in biomethane potential from liquids obtained from co-hydrothermal carbonization compared to liquids from hydrothermal carbonization of digested sludge without screenings in series 1, 2 and 3 - up to 60 %, 40 % and 26 % for three different sludges with initial total solids content of 2.6 %, 12.5 % and 21.5 % w/w.

1. Introduction

Wastewater treatment plants (WWTPs) generate three main by-products, found in primary effluents. The role of the sparse and dense grids within the mechanical part of the WWTPs is to separate the municipal waste called screenings (SC), which is which are the first group of by-products. Subsequently, gravel and sand separators collect the second fraction of waste materials. The role of pre-settlers is to separate the remaining suspended solids in the form of raw sludge (RS).

The biological stage of wastewater treatment is responsible for reducing organic compounds and nutrients, which produces excess biomass called activated sludge (AS). To ensure the functionality of biological reactors, the produced AS needs to be removed from the operation. The mixed RS and AS are defined as sewage sludge (SS) and form the third group of by-products [1]. In WWTPs, SS can be successfully used as feedstock in anaerobic digestion processes (AD) within biogas plants to form biogas and digested sludge (DS) [2].

According to Waste Classification [3], by-products generated at the WWTPs must be managed or disposed of. Sand and gravel can be

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Nomenclature

(AD)	Anaerobic digestion
(ADS)	Anaerobic digestion sludge
(AS)	Active sludge
(BMP)	Biomethane potential
(co-HTC)	Co-hydrothermal carbonization
(DS)	Digested sludge
(DW)	Dewatered sludge
(HC)	Hydrochar obtained from digested sludge
(HCSC)	Hydrochars obtained from mixed digested sludge with screening
(HTC)	Hydrothermal carbonization
(HHV)	Higher heating value
(L)	Liquids obtained in HTC from digested sludge
(LSC)	Liquids obtained in HTC from digested sludge and screening
(RS)	Raw sludge
(SC)	Screenings
(SS)	Sewage sludge
(TH)	Thickened sludge
(WWTPs)	Wastewater Treatment Plants

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washed, disinfected, and reused as an external feedstock. Screenings have a high organic waste content, therefore disposal in landfills is strictly prohibited. Due to their diverse composition, SC can be stabilized with other municipal waste however they are often incinerated, resulting in high disposal costs [4,5]. Digested sludge has favourable properties such as nutrient content and the potential to improve soil structure, therefore it is recommended to be used in agriculture applications, which is in line with the concept of a closed-loop economy [6,7]. However, there are concerns about inorganic micropollutants in the form of heavy metals, as well as uncontrolled organic pollutants such as pharmaceuticals and personal care products (PPCPs), pesticides, hormonal agents, that may have adverse effects on soil [8–10]. In addition, the high moisture content of DS (approximately 80 %) and the resulting high volume of sludge generated poses several challenges for the agricultural sector due to the limited availability of agricultural fields and limited fertilization opportunities during the winter [11]. To reduce the costs incurred for external sludge disposal, various methods of thermal treatment at WWTPs are being considered [12].

One of the promising methods for sludge conversion involves a combination of anaerobic digestion with a thermochemical process known as hydrothermal carbonization (HTC) [13–15]. The advantage of this system is the potential to convert wet digested sludge into a solid material known as hydrochar. The characteristics of hydrochar are: lower mass, lower moisture content, lower nitrogen, lower sulphur content, absence of biological contaminants, reduced levels of organic pollutants, reduced odour emissions and higher chemical stability, compared to untreated digested sludge [14,16–19]. In addition, studies carried out in laboratory settings [20], at a pilot scale [21] and industrial scale [22] have demonstrated the feasibility of biogas production from HTC liquids. Thus, this by-product could potentially be used as a co-substrate with sewage sludge in the anaerobic digestion but must comply with the principle of "Energy Efficiency (EE) First" [23] Moreover, produced gases mainly in the form of CO_2 can be effectively treated in the proposed system in situ [14]. Off-the-shelf technical solutions on an industrial scale can attract the attention of many WWTP operators worldwide. For the technology to be successfully implemented, the cost of external hydrochar management must compensate for the energy costs of the thermochemical process, however, energy targets for future years for 100 % renewable energy production [24], which will be included in the amendment of the Wastewater Directive [25], also need

to be considered. While energy recovery in the thermochemical process is progressive [26,27], the increased immobilization of heavy metals in hydrochar [28] poses a major challenge because it limits its further use in agriculture as mandated by the European directive (1986) that regulates the use of sewage sludge in agriculture [29]. In turn, in the energy sector, the use of hydrochar from digested sludge is limited due to the presence of heavy metals and low energy quality compared to the feedstock [30–32].

Recently, co-hydrothermal carbonization (co-HTC) processes involving mixtures of waste with sewage sludge or digested sludge have been noted in the literature as a low-cost process that can improve the quality of hydrochars and provide alternative fuels compared to dried sludge [33–46]. Co-HTC of various types of waste, including lignocellulosic biomass, non-lignocellulosic biomass, food waste, and plastic waste, often exhibit better energy properties than SS or DS and may also have synergistic effects, enhancing the final properties of hydrochars. This enhancement includes an increase in dry matter, volatile matter, fixed carbon, and higher heating value, as well as a decrease in ash and the concentration of heavy metals. However, such treatments can lead to increased levels of N or alkali metals in hydrochar, which can impact combustion quality [33,39,47]. Quality improvement in terms of nitrogen reduction can be achieved by additional measures such as the use organic solvents, however, such solutions can be costly [48,49]. Thus, to reduce costs, suitable wastes can be used, however, their availability may be limited for WWTPs. On the other hand, it is important to choose the right co-substrates to efficiently recover energy from co-HTC liquids during the anaerobic digestion process. Only a few studies have been conducted on how adding co-substrates affects the amount of methane produced from co-HTC liquids. Parmar et al. [33] showed a positive effect of certain biomass types such as woodchip and grass on the biomethane potential (BMP) from co-HTC liquids compared to HTC from DS. In contrast, Wang et al. [34,35] tested pine sawdust and showed no improvement in the BMP compared to HTC liquid from SS. Thus, further research is required to improve the quality of both HTC products.

As noted in the literature, there has been only one pilot-scale study [32] conducted on using screenings collected in the mechanical part of WWTPs to improve the higher heating value (HHV) of the hydrochars obtained through the co-HTC process with RS, AS, SS, and DS. Screenings are composed of different types of fractions such as lignocellulosic biomass, food waste, hygienic waste, textile waste, plastics, and other organic waste, making them a potential candidate for thermal and thermochemical treatment processes and are in line with a closed-loop economy [50–53]. Moreover, the ability to dispose of screenings in situ may be advantageous in terms of reducing the high cost of external disposal, improving the quality of hydrochars, and assuming a constant supply of co-substrates. The results of the study [32] showed an improvement in the HHV of hydrochars without considering the liquid and other important parameters of co-HTC products that are relevant to energy recovery. This article attempts, for the first time, to describe the overall impact of different fractions of screenings and digested sludge on the quality of co-HTC products and to assess the feasibility of disposing of the two wastewater treatment by-products without compromising the quality of HTC products. The concept of this study was, first, to characterize the quality of the obtained hydrochars using ultimate analysis and proximate analysis: moisture content, organic matter, volatile matter, ash content, and determination of ash fractions, including alkali metals, alkaline earth metals, and heavy metals. Second, to characterize and evaluate the liquids obtained in terms of biomethane production in laboratory BMP batch tests. The control samples in the BMPs were HTC liquids obtained from digested sludge.

2. Materials and methods

2.1. Feedstocks

Active digested sludge (ADS) before dewatering and dewatered

digested sludge (DW) were collected from the sludge dewatering station, while random screenings fractions (SC) were collected from the mechanical separation section of WWTPs in Ireland with a population equivalent estimated at 168,000. Thickened sludge (TH) was obtained by mixing ADS and DW in a mass ratio of 1:1. The sludges were stored at 4 °C, while the screenings were frozen. ADS was stored in the fridge for up to a week, then degassed and segmented. Prior to testing each measurement run, the screenings were defrosted, homogenized, and then mixed in a fixed mass proportion with the ADS, TH, and DW.

2.2. Hydrothermal carbonization setup and experiments

The experiments were conducted in three measurement series with three repetitions at each feedstock ratio. To limit changes in the total solid (TS) content of ADS during storage, the first measurement series included sludge from the ADS samples, the second from the TH samples, and the third from the DW samples. All tests were conducted at 200 °C and for 30 min in a 1-liter pressure reactor from PARR Instrument Company (model 4523, USA) equipped with an electric heating jacket and stirrer. The operating conditions were selected based on studies [15, 54–56] that had indicated a trade-off between the quality of hydrochar and the liquid's potential for biogas production.

The effect of additional screenings to digested sludge and resultant properties of HTC products with different initial moisture content ADS (2.6 % w/w), TH (12.5 % w/w), and DW (21.5 % w/w) were analysed. To study the effect of adding screenings to digested sludge at various mass ratios, the following proportions of screenings were incorporated: 3.3 %, 6.7 %, and 10 % w/w, and subsequently analysed.

The control samples were produced from HTC of ADS, TH, and DW without mixing with screenings. The selected screening fraction samples contained a mixture of food waste, plant biomass, hygienic waste, textile waste, and small fractions of plastics. The lowest proportion of screenings (3.3 % w/w) was selected based on information obtained from WWTPs regarding the amount of screenings generated relative to the amount of dewatered digested sludge obtained per year. Due to the variable composition of screenings, the highest proportion (up to 10 % w/w) was the maximum amount that would not cause technical problems in the HTC reactor. For each experiment, the initial mass of feedstocks was 300 g.

Continuous stirring at 100 RPM was applied from the start of the HTC process until the process was terminated after the reactor cooled to 25 °C. The resulting HTC slurry was weighed and separated using a vacuum filtration kit with filter paper parameters (Whatman Cat. No. 1004 110, 20–25 μm). The filtration time was 15 min. The obtained hydrochars from digested sludge (HC) and hydrochars obtained by mixed digested sludge with screening (HCSC) were weighed with the filter, dried at 45 °C, and stored for further analysis, while the obtained liquid from HTC digested sludge (L) and liquid obtained from HTC digested sludge with screening fractions (LSC) were weighed and stored prior to AD process. The gas content was calculated from the mass balance presented in section 2.4.

2.3. Analytical procedures

2.3.1. Digested sludge, screenings, hydrochars

Due to the high variability of screening fractions composition, experiments were conducted only for mixtures of screenings and ADS, TH, and DW. Thus, synergetic coefficients [39] were not presented in this research. Due to the high biohazard risks, the only physical property measured for screenings was total initial solids ($TS_{initial}$) in combination with ADS, TH, and DW. $TS_{initial}$ and the total solid final (TS_{final}) of hydrochars after filtration was determined using the PN-EN ISO 18134–3:2015–11. The ISO procedures 21656:2021 and 22167:2021 were used to determine the ash and volatile matter (VM) content, respectively. Ultimate analysis of chemical elements (C%, H%, N%) and S% was carried out using an 828 series elemental analyser (LECO

Corporation ISO-9001:2015). Alkali metals, alkaline earth metals and heavy metals were determined using inductively coupled plasma optical emission spectrometry ICP-OES (Agilent 5100) fitted with an SPS4 auto-sampler. Before conducting ICP-OES analysis, samples were washed at 550 °C, and digested with mixtures of nitric acid, hydrogen peroxide, and hydrofluoric acid in a microwave oven (Mars 6, CEM) according to the standard ISO 16967 and 16968. The calorific value of HHV (MJ/kg) was measured using a calorimetric bomb series 6200 Isoperibol (Parr Instrument Company).

2.3.2. HTC liquids and inoculum

The inoculum used for the batch laboratory tests was obtained from the outlet of the anaerobic digestion reactor at the WWTP and degassed over 5 days at 36 °C. To determine the biomethane potential (BMP) of HTC and co-HTC liquids, an automated AMPTS II system (Bioprocess Control AB, Lund, Sweden) was used. The studies were planned in three measurement series for ADS (1 series), TH (2 series) and DW (3 series) as presented in section 2.2. Prior to the experiments, the NPOC (Non-Purgeable Organic Carbon) contents of the inoculum and liquids were measured using a multi-N/C 3100 TOC analyser (Analytik Jena, Germany). The organic ratio (g NPOC/g NPOC) of inoculum to liquids (I/L) was 2 in a total working volume of around 400 ml in 500 ml bottles. The process temperature of all batch tests was 37 °C. The control parameters of the AD process were determined according to the methods described in APHA (American Public Health Association, Washington, DC (1999). These included measurement of pH and alkalinity (buffer capacity) using a pH meter (Cole Parmer Model No. 59002-00, UK), as well as volatile fatty acid (VFA) and ammonia ion concentration (N–NH$_4^+$) determined by steam distillation (BÜCHI K-355, Switzerland). The BMP tests were tested for 24 days according to the methodology defined in DIN 38414-S8 and VDI 4630. The end of the AD process was taken as the value of the daily biogas volume maintained for three days, which was less than 0.5 % of the total biogas volume produced.

2.4. Data processing and calculation

2.4.1. Mass balance

The content of the gas fraction (G) was estimated based on the average mass difference between the feedstock and the HTC slurry:

$$G\ (\%) = \frac{m_{feedstock} - m_{slurry}}{m_{feedstock}} \cdot 100\% \tag{1}$$

The mass balance also includes the average mass loss resulting from the separation of the HTC slurry:

$$\text{Mass loss}\ (\%) = \frac{m_{slurry} - m_{hydrochar} - m_{liquid}}{m_{feedstock}} \cdot 100\% \tag{2}$$

2.4.2. Feedstock and hydrochar

The properties of feedstocks and hydrochars were calculated based on the following equations:

$$FC_{db}\ (\%) = 100\% - \text{Ash}\ (\%) - \text{VM}\ (\%),\ db \tag{3}$$

$$O\ (\%) = 100\% - C\% - H\% - N\% - S\% - \text{ash}\% \tag{4}$$

$$HHV_{theoretical}\ (MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151\ N - 0.0211\ \text{Ash} \tag{5}$$

$$\text{Yields}\ (\%) = \frac{TS_{hydrochar} \cdot M_{hydrochar}}{TS_{Feedstock} \cdot M_{Feedstock}} \cdot 100\% \tag{6}$$

where TS – total solid (w/w), FC– fixed carbon M – mass of sample, VM – volatile matter, db – dry basic.

2.4.3. Liquids

To determine the BMPs of the liquids, the cumulative methane production (y) from the sample with inoculum (ml CH$_{4(sample + inoculum)}$)

and from the incubated inoculum (ml CH$_{4(inoculum)}$) were measured. The study used an inoculum-to-substrate ratio (I/S) of = 2:1 as recommended by Villamil et al. [57], thus the values of biogas production efficiency are reported in terms of the amount of organic matter added as liquids to the inoculum.

$$BMP_{exp}\ (ml\ /\ g) = \frac{ml\ CH_{4\ (sample+inoculum)} - ml\ CH_{4\ (inoculum)}}{g(NPOC)_{sample\ add\ to\ flask}} \quad (7)$$

Modified Gompertz equation [35] was used for the calculation of the kinetic parameter of AD:

$$y = P \cdot exp\left\{ - exp\left[\frac{R_m \cdot e}{P} \cdot (\lambda - t) + 1 \right] \right\} \quad (8)$$

y –the cumulative methane production, Nml CH$_4$/g Non-purgeable organic carbon (NPOC)

P – potential methane production, ml CH$_4$/g NPOC.

R$_m$ – maximum rate of methane production, mL CH$_4$/(g NPOC d)

λ – lag time phase, d

t – measured time, d

e − base of the natural logarithms, namely 2.71.

3. Results and discussion

3.1. Mass balance

The effect of the amount of screenings in the ADS, TH and DW feedstocks in the co-HTC process on the distribution of products between the solid, liquid and gas phases is shown in Fig. 1 and in Tables S–1. (Supplementary material). The primary factor affecting product distribution was the TS$_{initial}$. Higher TS$_{initial}$ of TH and DW feedstocks resulted in higher hydrochar production and lower liquid production. In contrast, a slight increase in gas yields, relative to ADS and TH was observed only for DW. Overall, the addition of SC% had little effect on product distribution. The only notable differences were observed for HCSC ADS where an increase in SC% led to a slight increase in the amount of hydrochars and gases and a decrease in the amount of liquid produced. This can possibly be attributed to the TS$_{initial}$ associated with the mixture of ADS and screenings, which was higher than for ADS without screening as shown in Table 1. No significant differences in TS$_{initial}$ were observed for TH and DW. It was also noted that fluctuations in HCSC and LSC (liquids obtained in HTC from digested sludge and screening) from DW production may have been caused by the unreacted screenings fractions.
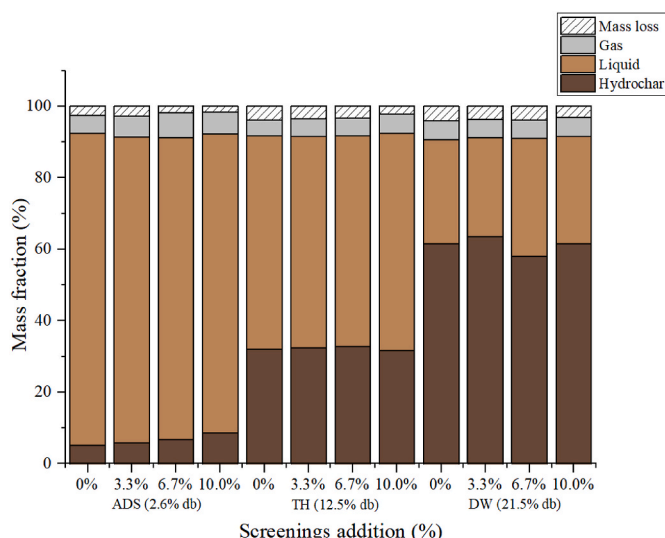

Fig. 1. Distribution of HTC and co-HTC products.

3.2. Hydrochar and liquids characteristic

3.2.1. Effect of screenings addition on technical parameters of hydrochars

Table 1 shows the physicochemical properties of the feedstocks and hydrochars considered as solid fuels, whereas

Table 2 shows the properties and potential of liquids as substrates in the AD process.

The TS$_{final}$ values of HC and HCSC were relatively low, as the dewatering efficiency depended on the type of laboratory equipment and the dewatering method [21,46]. The measurement of TS$_{final}$ was intended as a general evaluation of the effectiveness of co-HTC in dewatering solid products. Thus, the addition of SC% (Fig. 2) improved the final dewatering of HCSC ADS, TH, DW relative to HC. However, an increase in SC % content above 6.6 % w/w resulted in a slight decrease in TS$_{final}$ for ADS and DW HCSC.

The initial values of VM, ash, and FC can differ for feedstocks collected at the sludge dewatering station (Fig. 2). This due to the dewatering process, leading to a loss of ash in the filter press leachate or an increase in the VM fraction after the addition of dewatering organic polyelectrolytes [30]. In HC ADS, TH, DW, a general increase in ash compared to feedstock (Fig. 2) can be observed mainly through the loss of the VM fraction due to dissolution of organic matter in subcritical water during HTC. In hydrochars from co-HTC processes, ash content and VM show an opposite trend, with a gradual decrease in ash and a gradual increase in VM for HCSC TH and DW as SC% increases, while for HCSC ADS with low sludge concentration, a rapid decrease in ash and a rapid increase in VM% were observed. Such a result suggests low ash content and high VM in the tested screenings fractions compared to sludge. Similar results were obtained in other studies [33,37,58]. For example, Parmar et al. [33] tested DS with grass, privet hedges and woodchip and had similar observation decrease in ash, as well as an increase in VM. Other studies conducted with pine sawdust [34], food waste [36], and PVC waste [40] with sewage sludge confirm these trends. Thus, regardless of the fractions present in the screenings, the same correlations could be observed.

When the same waste mixtures were subjected to higher process temperatures, regardless of the type of co-substrates used [33,34,36], it resulted in an increase in the ash fraction. This increase was due to the degradation of VM towards gases (outgassing), liquids (degradation and solubility of organic matter), as well as towards the formation of secondary fractions (secondary carbonization) of hydrochars [59]. This interaction of dissolved intermediates was also manifested by an increase in FC. Based on studies [33–46,59] conducted on co-HTC of sludge, it is suggested that the increase in FC % in hydrochars can be attributed to three main factors. Firstly, the initial FC% in the co-substrate used is higher. Secondly, there is an enhanced reaction and interaction of substrate intermediates as the severity of the reaction increases. Lastly, there can be a synergistic effect under the same reaction conditions. Due to relatively mild conditions, FC% were initially lower for HC ADS, TH, and DW compared to feedstocks, probably due to the dissolution of some organic components in the liquid and insufficient activation energy to initiate secondary carbonization. As the proportion of screenings in the co-HTC process increased, an increase in FC% was observed in most cases. Similar trends for HTC followed by co-HTC were observed in studies [36,39], while in other studies an increase in FC after both HTC and co-HTC was observed [33,37,40].

Mahata et al. [59] presented two scenarios for the effect of biomass/sludge mixing ratio on HC yield: 1) the higher the biomass/SS ratio, the higher the organic content, the lower the ash content, and thus the decrease in hydrochar yield. 2) the higher the biomass/SS ratio, the higher the concentration of lignin present in the biomass and thus the increase in hydrochar yield. Scenario 1. can be observed for HCSC ADS with low sludge concentration (Fig. 2), in which the dominant fraction is screenings containing less ash but a higher organic fraction. On the other hand, when the SC% increase, a slight increase in yields HCSC (3.3 % w/w) could also be observed (Fig. 2). As mentioned, due to the relatively

Table 1
Properties of digested sludge and hydrochars produced in HTC and co-HTC process.

Material	Process parameters		Proximate analysis					Energy properties	Ultimate analysis					
	Screenings addition	$TS_{initial}$	TS_{final}[b]	Yields	Ash	VM	FC	$HHV_{(exp)}$	C	H	N	S	O	$HHV_{(teor)}$
	[%] db[a] w/w	[%]	[%]	[%]	[%] db[b]	[%] db	[%] db	[MJ/kg] db	[%] db	[%] db	[%] db	[%] db	[%] db	[MJ/kg] db
ADS	–	2.58 ± 0.01	–	–	37.49 ± 0.86	54.28 ± 0.02	8.23 ± 0.11	13.30 ± 0.16	28.06 ± 0.02	3.15 ± 0.19	4.28 ± 0.02	1.35 ± 0.02	26.21 ± 0.65	10.07 ± 0.21
HC	0.0	2.58 ± 0.01	30.05 ± 2.20	58.66 ± 0.48	55.42 ± 0.43	41.98 ± 0.08	2.60 ± 0.34	11.37 ± 0.37	26.98 ± 0.12	2.60 ± 0.02	2.08 ± 0.01	0.84 ± 0.01	12.90 ± 0.69	10.04 ± 0.05
HCSC	3.33	3.01 ± 0.11	34.25 ± 3.06	65.61 ± 4.33	38.84 ± 1.09	57.10 ± 2.04	4.06 ± 1.01	12.77 ± 0.56	32.49 ± 0.51	3.03 ± 0.06	1.72 ± 0.06	0.78 ± 0.03	23.14 ± 0.73	11.76 ± 0.15
HCSC	6.67	3.92 ± 0.23	34.88 ± 1.10	60.34 ± 4.60	31.94 ± 0.26	62.25 ± 0.61	5.81 ± 0.54	15.57 ± 0.55	36.35 ± 0.29	3.17 ± 0.07	1.62 ± 0.13	0.75 ± 0.02	26.17 ± 0.35	13.04 ± 0.21
HCSC	10.00	5.24 ± 0.18	33.26 ± 1.17	54.83 ± 1.40	28.41 ± 1.88	66.26 ± 0.48	5.34 ± 1.54	18.06 ± 0.24	39.34 ± 0.28	3.31 ± 0.06	1.49 ± 0.12	0.67 ± 0.03	26.79 ± 1.87	14.17 ± 0.24
TH	–	12.54 ± 0.22	–	–	34.30 ± 0.16	58.93 ± 0.16	6.76 ± 0.04	15.00 ± 0.10	31.67 ± 0.09	5.12 ± 0.02	4.72 ± 0.01	1.62 ± 0.01	22.57 ± 0.28	14.12 ± 0.09
HC	0.0	12.54 ± 0.22	25.19 ± 1.59	65.50 ± 2.30	47.35 ± 1.13	47.05 ± 0.54	5.60 ± 0.79	14.69 ± 0.31	30.93 ± 0.12	4.15 ± 0.07	3.38 ± 0.03	1.50 ± 0.03	12.69 ± 1.07	13.48 ± 0.09
HCSC	3.3	12.14 ± 0.33	27.61 ± 0.72	73.87 ± 1.29	46.57 ± 0.24	50.31 ± 0.35	3.12 ± 0.56	15.17 ± 0.34	32.33 ± 0.17	4.05 ± 0.11	3.31 ± 0.02	1.41 ± 0.04	12.33 ± 0.14	13.90 ± 0.07
HCSC	6.6	12.31 ± 0.92	27.70 ± 1.53	73.37 ± 1.03	42.70 ± 0.71	51.23 ± 0.50	6.07 ± 0.47	16.49 ± 1.29	33.33 ± 0.49	4.11 ± 0.20	3.11 ± 0.14	1.39 ± 0.01	15.36 ± 0.69	14.09 ± 0.39
HCSC	10.0	12.64 ± 0.12	30.96 ± 1.54	77.72 ± 2.67	40.51 ± 0.31	52.47 ± 0.70	7.02 ± 1.06	17.63 ± 0.23	33.87 ± 0.21	3.97 ± 0.34	3.05 ± 0.08	1.33 ± 0.01	17.28 ± 0.59	13.95 ± 0.41
DW	–	21.53 ± 0.21	–	–	35.32 ± 0.03	59.89 ± 0.42	4.79 ± 0.39	14.13 ± 0.42	31.07 ± 0.09	5.45 ± 0.05	4.75 ± 0.01	1.73 ± 0.01	21.77 ± 0.14	14.38 ± 0.04
HC	0.0	21.53 ± 0.21	27.54 ± 1.11	78.64 ± 2.32	45.38 ± 0.19	51.06 ± 0.27	3.56 ± 0.27	15.56 ± 1.53	32.10 ± 0.36	4.64 ± 0.08	4.35 ± 0.07	1.70 ± 0.09	12.10 ± 0.75	14.59 ± 0.29
HCSC	3.3	21.43 ± 1.24	27.57 ± 0.23	81.79 ± 0.25	43.47 ± 0.38	52.10 ± 0.45	4.43 ± 0.32	15.11 ± 0.21	33.00 ± 0.71	4.57 ± 0.06	4.24 ± 0.04	1.65 ± 0.04	12.82 ± 1.01	14.79 ± 0.23
HCSC	6.6	21.16 ± 0.28	28.62 ± 0.74	78.45 ± 0.61	41.84 ± 0.38	52.91 ± 0.03	5.25 ± 0.40	16.06 ± 0.14	33.47 ± 0.09	4.59 ± 0.14	4.11 ± 0.17	1.60 ± 0.02	14.09 ± 0.65	14.84 ± 0.19
HCSC	10.0	21.01 ± 0.34	27.89 ± 1.72	81.19 ± 2.42	40.25 ± 1.44	53.58 ± 0.19	6.17 ± 1.29	16.13 ± 0.13	33.47 ± 0.39	4.43 ± 0.30	4.35 ± 0.25	1.60 ± 0.01	13.06 ± 1.24	14.51 ± 0.42

[a] Dry basis.
[b] After 15 min vacuum filtration.

low process temperature, the screenings may have contained unreacted lignin fractions from the plant biomass identified in the screenings or refractory textile fractions, which usually require higher degradation temperatures [60]. In the case of HC DW, irregular trends were observed as in the case of hydrochar production, due to the presence of unreacted fractions.

The HHV, both measured and calculated, are summarized in Fig. 3. The differences in HHV_{exp} and HHV_{teor} observed in series 1, 2, and 3 may have been due to the different fractions of hydrochar and different sample sizes used in the elemental analysis (0.2g) and calorimetric bomb (1g). However, the difference in values of ADS and HC ADS analysed cannot be explained by this. The feedstocks had different initial HHV due to the modified composition after the filter press. The HTC process caused a decrease in HHV for HC ADS and a slight decrease for HC TH, while for HC DW, a slight improvement. Hence, the type of filtration and polyelectrolytes added could play an essential role in planning and optimizing HTC processes on WWTPs. An increase in SC% contributed to

an increase in HHV_{exp} in HCSC, which was closely related to an increase in VM% as well as FC% and a decrease in ash%. Therefore, regardless of the fraction, screenings showed superior properties in comparison to DS, and showed an improvement in the quality of hydrochar.

3.2.2. Chemical analysis of feedstock, HTC, and co-HTC products

Digested sludge can consist of bioresistant fractions of cellulose, proteins, humic substances, and lignin, but especially of predominantly extracellular polymeric substances (EPS) produced by bacteria [14]. These fractions typically require high HTC degradation temperatures, low pH and, in the case of EPS, an extremely alkaline environment. The main reaction pathways occurring during HTC/co-HTC can be represented by a Van Krevelen diagram (Fig. 4). Lower molar ratios of O/C and H/C compared to feedstock indicate dehydration and decarboxylation reactions of DS components. Dehydration is characterized by the elimination of hydroxyl groups toward water formation, while decarboxylation is characterized by the elimination of carboxyl groups

Table 2

Properties of HTC and co – HTC liquids.

Material	Process parameter		Liquids properties as substrate to AD				
	Screenings addition	$TS_{initial}$	$NPOC^b$	$N-NH_4^+$	VFA	pH	Alkalinity
	[%] w/w	[%]	[g/l]	[g/l]	[g/l]	–	[g/l]
ADS	–	2.58 ± 0.01	3.76 ± 0.54	1.06 ± 0.02	0.81 ± 0.02	7.65 ± 0.07	3.27 ± 0.01
L ADS	0.00	2.58 ± 0.01	4.39 ± 0.06	1.23 ± 0.03	2.71 ± 0.62	7.54 ± 0.14	3.41 ± 0.32
LSC	3.33	3.01 ± 0.11	4.85 ± 0.10	1.37 ± 0.03	2.71 ± 0.57	7.51 ± 0.01	3.35 ± 0.05
LSC	6.67	3.92 ± 0.23	5.55 ± 0.30	1.44 ± 0.03	3.02 ± 0.43	7.43 ± 0.02	3.33 ± 0.10
LSC	10.00	5.24 ± 0.18	6.03 ± 0.28	1.37 ± 0.06	4.11 ± 0.09	7.30 ± 0.04	2.99 ± 0.23
L TH	0.0	12.54 ± 0.22	15.29 ± 0.83	2.60 ± 0.10	2.83 ± 0.67	7.37 ± 0.02	3.74 ± 0.14
LSC	3.3	12.14 ± 0.33	16.15 ± 0.96	2.72 ± 0.03	4.66 ± 0.49	7.23 ± 0.06	4.04 ± 0.09
LSC	6.6	12.31 ± 0.92	15.49 ± 0.36	2.75 ± 0.02	4.43 ± 0.42	7.33 ± 0.07	4.10 ± 0.10
LSC	10.0	12.64 ± 0.12	15.69 ± 0.70	2.55 ± 0.03	3.86 ± 0.54	7.22 ± 0.01	3.58 ± 0.20
L DW	0.0	21.53 ± 0.21	26.20 ± 0.79	4.30 ± 0.25	5.57 ± 0.54	7.65 ± 0.16	6.30 ± 0.32
LSC	3.3	21.43 ± 1.24	25.55 ± 0.36	4.59 ± 0.10	7.00 ± 0.26	7.65 ± 0.03	6.15 ± 0.12
LSC	6.6	21.16 ± 0.28	26.36 ± 0.98	4.44 ± 0.21	8.11 ± 1.29	7.64 ± 0.11	5.57 ± 0.50
LSC	10.0	21.01 ± 0.34	25.34 ± 0.36	4.47 ± 0.07	7.77 ± 0.30	7.49 ± 0.08	5.47 ± 0.16
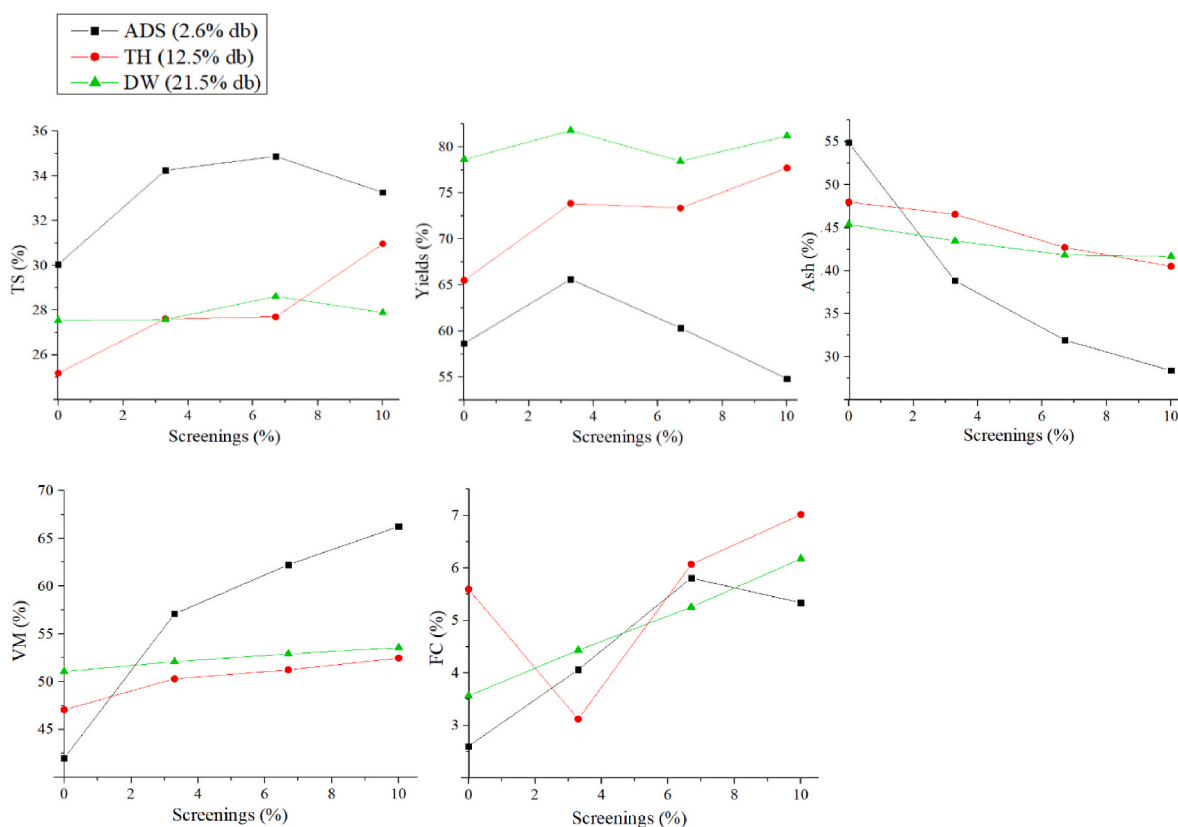
Fig. 2. Effect of screenings content in ADS (2.6 % w/w), TH (12.5 % w/w), DW (21.5 % w/w) on technical parameters of hydrochars after HTC process.

toward CO_2 [16].

After HTC treatment, a decrease in the carbon content of the HC ADS structure could be observed, a slight decrease for HC TH, and a slight increase for HC DW (analogous to the HHV_{exp}). Thus, the carbonization processes may have depended on the type of material obtained from WWTPs and its $TS_{initial}$ content. As can be seen from Tables 1 and 2 the water/sludge ratio had a significant impact not only quantitatively, but also qualitatively. For example, the highest release of carbon and nitrogen from ADS to the liquid (with the highest water content) could suggest enhanced hydrolysis of organic components, decarboxylation (Fig. 4) and subsequent deamination of e.g. proteins (increase in N – NH_4^+ and VFA in the liquid (Fig. 5). Despite the lower N reduction in HC TH and DW compared to HC ADS, higher concentrations of N – NH_4^+ and VFA in the liquids (Fig. 5) were observed, due to the higher $TS_{initial}$ and

lower production of HTC liquids. Parallel dehydration reactions during HTC may have been related, for example, to the dehydration of some polysaccharides contained in ADS, but also to the reduction of other bound water. However, the O/C ratios are much lower than H/C for HC ADS, TH and DW, so the main reaction pathway during HTC of DS may have been decarboxylation. Similar trends were shown by Parmar et al. [33], who noted that decarboxylation processes mainly accompany feedstocks with high inorganic content (SS, DS), while dehydration accompanies feedstocks with lower ash content. (e.g., lignocellulosic biomass).

The addition of screenings increased the C, FC and HHV content of HCSC ADS, TH and DW, which was a common phenomenon observed during co-HTC processes with sewage sludge and digested sludge for various co-substrate [59]. The increase in carbon content in the HCSC
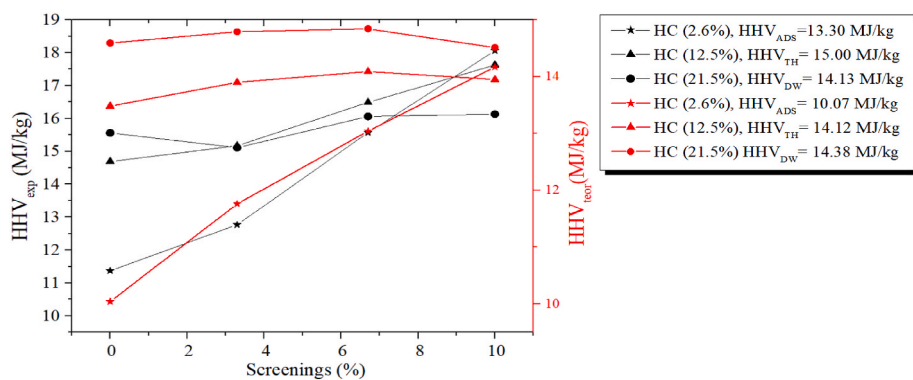
Fig. 3. Effect of screenings content in ADS (2.6 % w/w), TH (12.5 % w/w), DW (21.5 % w/w) on HHV of hydrochars.
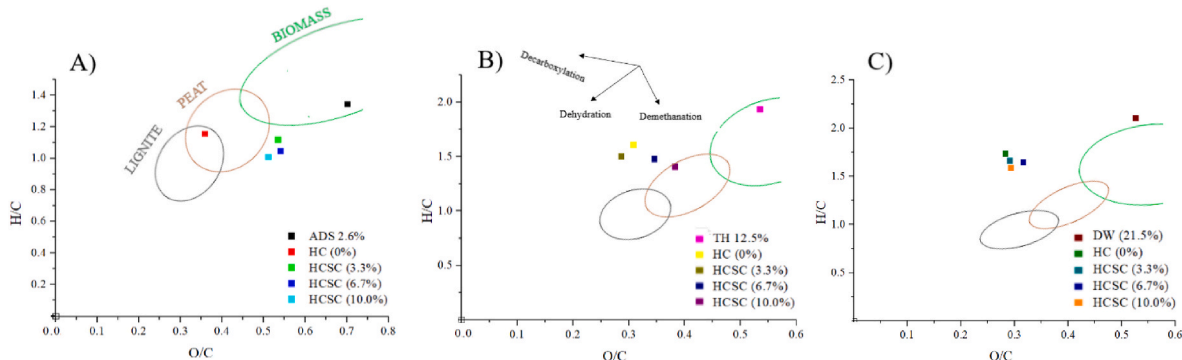

Fig. 4. Van Krevelen diagram: A) screenings addition to ADS (2.6 w/w), B) screenings addition to TH (12.5 % w/w), C) screenings addition to DW (21.5 % w/w).
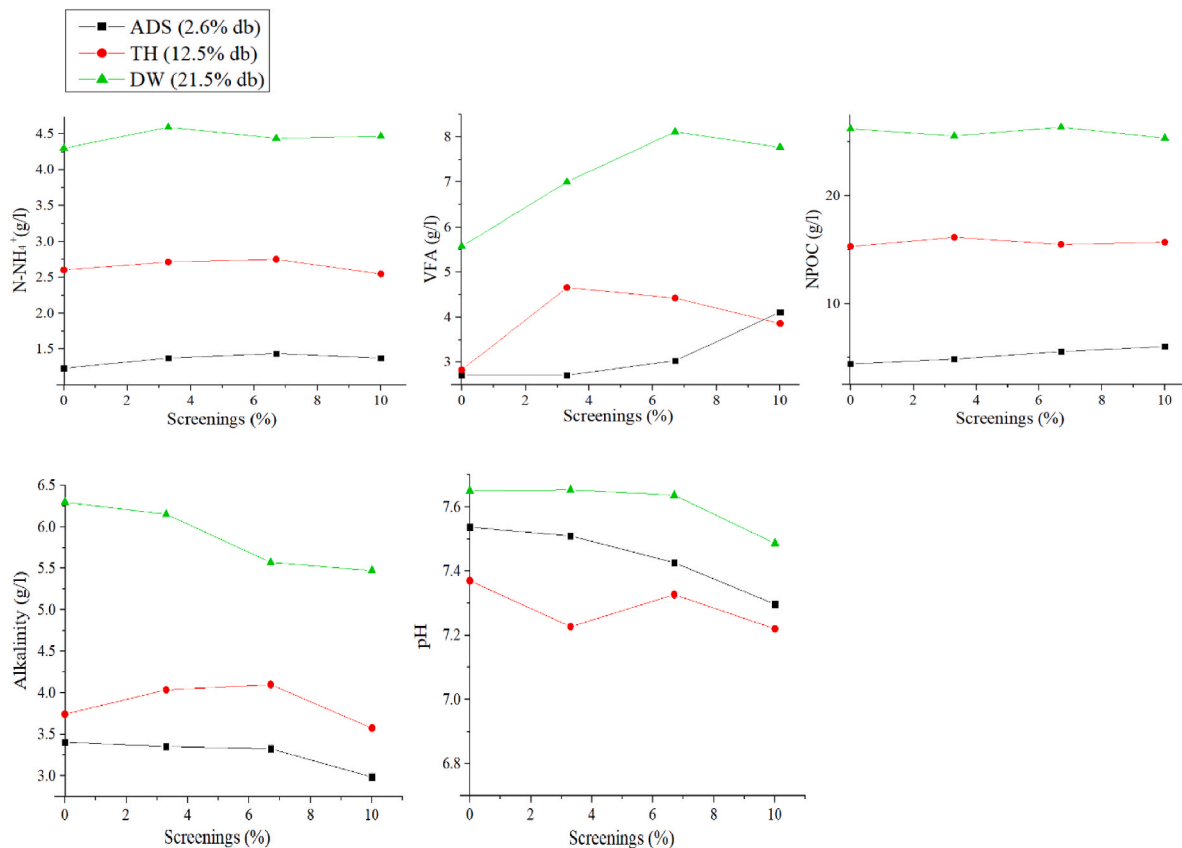

Fig. 5. Effect of screenings content in ADS (2.6 % w/w), TH (12.5 % w/w) and DW (21.5 % w/w) on liquids composition after HTC process.

structure may have been related to the possibility of hydrolysis and subsequent secondary carbonization of some screening intermediates under mild reaction conditions. For example, studies conducted on co-HTC of food waste and SS showed that carbohydrates, lipids, and proteins contained in food waste could hydrolyse under lower process conditions [36]. The same was observed for lignocellulosic biomass, whose components dehydrated faster than proteins contained in sludge [59]. Such results are consistent with observations of an increase in VFA in LSC, with an increase in the proportion of screenings (Fig. 5) as a result of the dehydration reaction (Fig. 4). Similar trends are evident showing the gradual increase in carbon and FC in the hydrochar due to the potential polymerization of intermediates derived from polysaccharides (e.g., in the form of hydroxymethylfuraldehyde (HMF), furan) into the aromatic structures of the hydrochar.

Both the feedstock and HTC liquids were characterized by a slightly alkaline pH. With increasing SC%, the pH decreased slightly, which was consistent with the increase in VFA, constant ammonium nitrogen content, but also this could be due to the acidic intermediates soluble in the liquid [35,59]. According to literature, co-HTC processes were characterized by synergistic effects in the form of Maillard reactions occurring between reduced sugars and amino groups of amino acids contained in sludge proteins, which could form heterocyclic nitrogen structures in hydrochars at temperatures above 180 °C [59]. In this study, only a slight increase in nitrogen content was observed for HCSC DW at the highest concentration of screenings, which could be related to the higher concentration of sludge-derived amino acids and screenings-derived sugars that enhanced such interactions.

The values of H/C and O/C molar ratios allow a preliminary comparison of the properties of feedstocks and hydrochars with other fuels. In addition, the specific molar ratio acts as an indicator [38]. A low O/C ratio value indicates higher hydrophobicity, while a low H/C ratio can indicate higher aromaticity and energy efficiency of the fuel. According to the Van Krevelen diagram, only hydrochars with HC (0 %) from ADS (2.6 %) and HCSC (10 %) from TH (12.5 %) (Fig. 4) had similar properties to lignite and peat. In general, HC and HCSC had higher hydrophobicity and higher aromaticity compared to feedstocks. HCSCs, on the other hand, had lower H/C values compared to HCs and were characterized by higher energy density. Increasing the amount of screenings resulted in higher VM. However, fuels with a high content of VM have a less stable flame, burn faster, and may emit more gaseous pollutants during combustion. Also, N and S % were important as they generate pollutants in the form of NOx and SOx during combustion [14]. HCSCs in the ADS group had the lowest levels of N and S, implying that screenings added had either no or lower amounts of such pollutants. The same trend was observed for HSCS TH and DW. However, one would also have to consider the potential Maillard reactions that could occur for a higher proportion of screenings than 10 % w/w. On the other hand, the source of the higher S content in the TH and DW feedstocks, compared to ADS, could have been the addition of conditioning agents to aid dewatering on the filter press, and thus S contaminants could have been controlled by the WWTPs' operator.

3.3. Effect of screenings addition on ash composition and elemental distribution between hydrochar and liquid

The analysis and monitoring of heavy metals (HMs), alkali metals, and alkaline earth metals contained in modified hydrochar is important in terms of combustion process conditions, sinter formation, emissions, and thus flue gas cleaning efficiency. Tables S–2 (**supplementary material**) shows the distribution of elements contained in sludge between the solid and liquid phases of the HTC/co-HTC process. Digested sludge has a high concentration of alkali and alkaline earth metals, which on the one hand can cause operational problems related to corrosion of structural materials, while on the other hand they can act as catalysts. Moreover, elements such as K lower the melting point of ashes, contributing to unfavourable sintering, while Ca contents can raise the

melting point [33]. According to Figure F-1 (**supplementary material**), the content of, Na, K, Mg and Ca in the hydrochar decreases with increasing SC%. (except for Mg in HCSC ADS, and Ca in HCSC TH). For HTC liquids, the trends are different, i.e. for alkali metals a decrease in concentration is observed, while for alkaline earth metals an increasing trend can be observed.

The EU directive on the permissible contents of heavy metals (Cd, Cu, Ni, Pb, Zn, Hg, Cr) in sludge mainly concerns land applications from WWTPs [11]. In the case of combustion processes, HMs such as As, Hg, Cd and Pb should be particularly controlled due to the difficulty of flue gas treatment. Elements in the sequence Zn > Cu > Cr > Ni > Pb/As were detected in the feedstocks and hydrochars (Fig. 6.). The content of all HMs in feedstock and their hydrochar met the requirements for potential use in agriculture or soil remediation purposes. No Cd and Hg were found in the solid and liquid samples. In other studies, similar sequences in the feedstocks were observed with values in the same order [40,42,43]. Regardless of the sludge types, the HTC processes of the three sludge types caused to an increase in HM concentrations in hydrochar, which is consistent with other observations and results on HM distribution [40,42,43].

Screenings, because of their origin (e.g. industrial waste), may contain heavy metals and pose a potential hazard. However, during the co-HTC experiments, in most cases, a decrease in HM concentrations was observed as the content of the screenings increased (**Table S-2 – supplementary material**), and thus, the screenings either contained no or lower concentrations of HM compared to the sludge. A similar dilution effect was observed in other studies using co-substrate with lower HM contents [42]. However, in some studies, the phenomenon of increased immobilization of heavy metals by the synergistic effect of co-substrate was observed, despite lower HM contents in the hydrochars obtained from sludge and co-substrate e.g. for Ni and Cr [40]. In this study, such a phenomenon was observed for individual cases also for Ni in HCSC (10 % w/w) with ADS and HCSC (3.3–6.7 w/w) with DW, as well as for Pb in HCSC (3.3–10 % w/w) and As in HCSC (6.7 % w/w). The key findings noted that when the co-substrate was added, the As content also changed [40]. Additionally, the addition of random screening fractions may have directly affected the increase of HM in some samples. It is important to note that heavy metals (Cr, Ni, Zn, As) have low solubility in water under basic conditions [59] or they may not dissolve at all (Pb, Cu). As a result, low concentrations of HM in the liquids, which were often within the margin of error, made it difficult to make clear observations and conclusions about the effect of co-substrate addition in the co-HTC process.

3.4. Potential of liquids in AD process

3.4.1. Methane production characteristics

The results of cumulative methane production (y) and daily methane production (DMP) obtained after 24 days of experiments from series 1, 2 and 3 are shown in Fig. 7. Calculated values of BMP_{exp} are shown in Table S-3 (supplementary material). The relatively small differences in the biogas produced from the liquids compared to the incubated inoculum were due to the high $I/S = 2$ ratio, as well as high concentrations of NPOC in the liquids and low values for the inoculum. The combination of these factors led to a small amount of substrate being used in the batch fermentation tests. The highest level of methane production was consistently observed on the first day of the process, regardless of the series of tests conducted. A similar effect, i.e. high methane production immediately after inoculation and thus a reduction in the time required to reach the exponential phase, was observed in another work [61–63]. The highest average DMP values were obtained for LSC (10%w/w) in series 1 and 3, while LSC (6.67 % w/w) in series 2. In contrast to the highest DMP and average BMP values were obtained for LSC (6.67 % w/w) in series 1 and 3, and LSC (10 % w/w) in series 2 (Fig. 8).

Most of the average BMP for a given co-HTC experiment were higher than the average BMP values for their L (0) control samples. In contrast, the highest possible rate was obtained for TH with 10 % screenings at
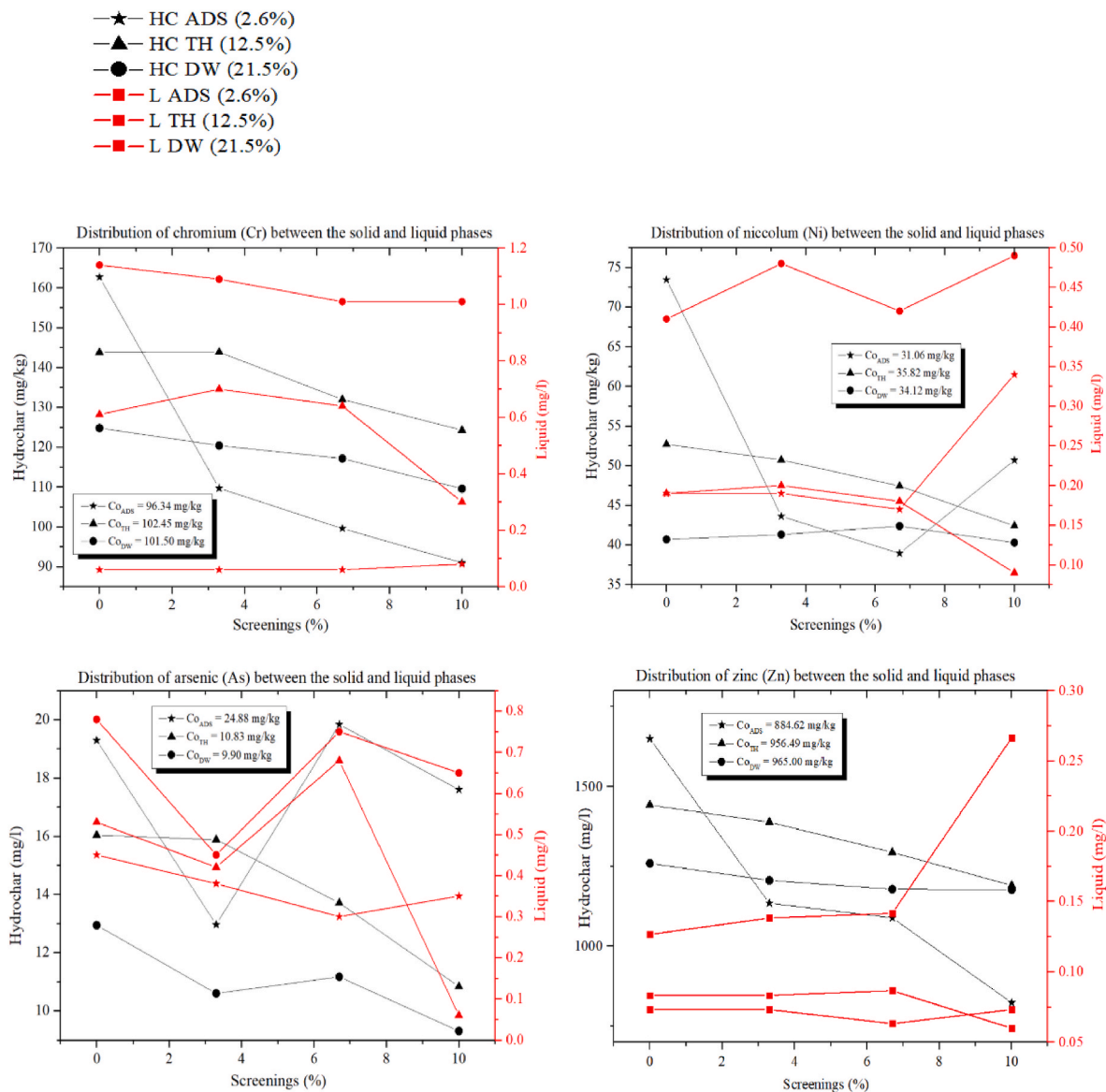
Fig. 6. Effect of screenings content in ADS (2.6 % w/w), TH (12.5 % w/w), DW (21.5 % w/w) on heavy metal distribution between hydrochar and liquids.

338 mlCH4/g NPOC, which could also be related to the highest BMP (240 mlCH4/g NPOC) for the control sample in series 2. Thus, the type of modified feedstock also has an important role in the AD process. A general improvement in the BMP in the co-HTC process of sludge digested with a variety of biomass: 1) grass, 2) privet hedge 3) woodchip in a 1:1 ratio was also observed by Parmar et al. [33]. Wang et al. [34, 35]. On the other hand, for liquids from HTC of sludge and sawdust showed the highest potential for HTC liquid from SS without sawdust at 311 mlCH4/g COD and comparatively 294 mlCH4/g COD for low reaction conditions (160°, 2h, 9.1 % w/w) and a substrate mass ratio of 1:1. The addition of co-substrate did not show any positive effect on methane production from liquid as the other BMP values were lower.

It is difficult to compare the results obtained in this study with literature data as studies related to methane potential of the feedstock (screenings) are non-existent. In the discussion of the results, one can only refer to the methane potential of the HTC liquid from sewage sludge, for which methane yields vary from 0.022 to 0.325 L CH4/g COD. Several factors also influence methane yields such as: carbonization conditions, inoculum acclimation, I/S ratio, initial feedstocks characteristics, nutrients concentration etc [54,64]. In the conducted research, an alternate approach was adopted for measuring COD in HTC liquids due to the methodological limitations analysing this indicator, such as: lack of distinction between organic and inorganic carbon, interference of other compounds (like nitrites, bromides, iodides, metal ions and sulphur) and the generation of toxic waste (dichromate). However, if the conversion factor of TOC in COD ranges from 2.5 to 4 depending on the wastewater, dividing the obtained methane yields by 4, the indicative data is still within the range of methane production for HTC liquids from sewage sludge.

3.4.2. Gompertz model data analysis

Kinetic parameters estimated based on the modified Gompertz model are summarized in Tables S–3 **(supplementary material)**. The high determination coefficient (R^2 ranged from 0.996 to 0.999) values indicate that the model fits very well with the experimental data. However, the percentage difference between predicted and experimental methane yields varies over quite a wide range, and extreme values are reported for each test series. By disregarding the anomalous results, the mentioned parameter (%Δ) (Table S3 -supplementary material) for the first series ranges from 0.85 to 14.62 %, and for the second and third series, from 6.32 to 14.51 % and from 0.001 to 3.33 %, respectively. In rare cases, the parameter value exceeds 10 %, which suggests that the
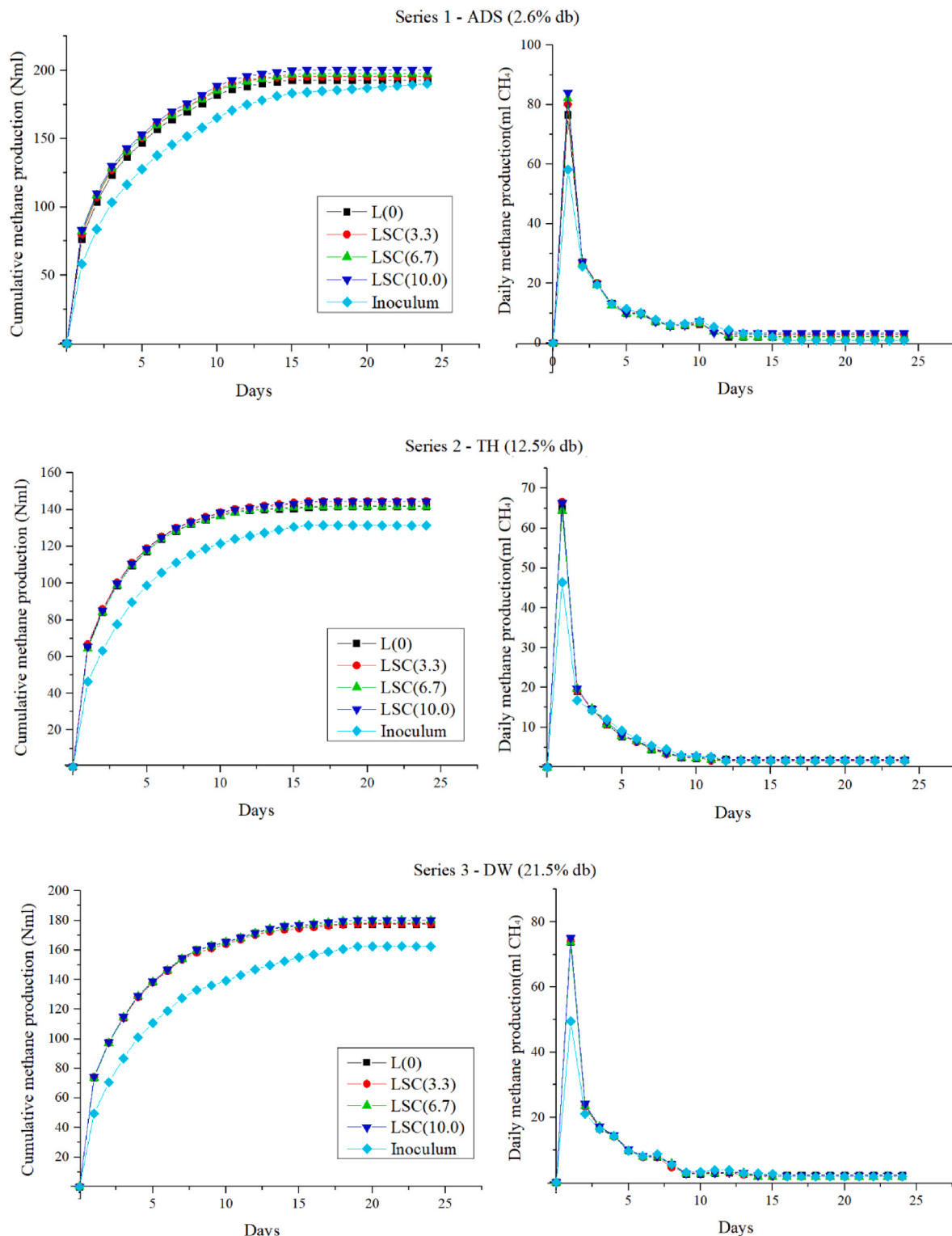
Fig. 7. Effect of screenings content in ADS (2.6 % w/w) – series 1, TH (12.5 % w/w) – series 2, and DW (21.5 % w/w) – series 3 on methane production from liquids after HTC process.

modified Gompertz model can be successfully used to predict the methane potential of HTC liquid and co-HTC liquids [63].

The lag time phase (λ) values estimated by the modified Gompertz model ranged from −3.51 d to −2.26 d for the tested samples. This indicates that tested feedstock did not inhibit the process, and the bacteria did not need time to adapt to the substrates and effectively used the soluble organic substance contained in the liquid phase to produce

methane [65]. Moreover, Chu et al. [66] reported that negative values in the lag phase correspond to a well-selected inoculum and an easily biodegradable feedstock. It is also worth emphasizing that in most cases the lag phase values were lower for co-HTC liquids than for control samples (without screenings), which may be another advantage of using screenings as co-substrate in the co-HTC process.
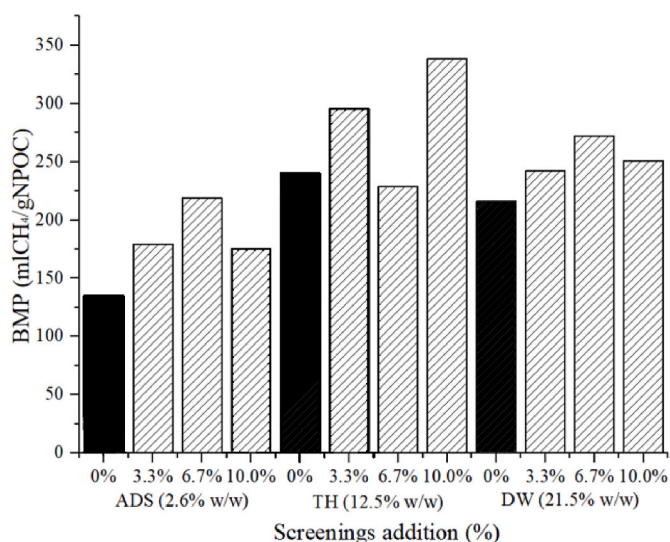
Fig. 8. Effect of screenings content in ADS (2.6 % w/w), TH (12.5 % w/w), and DW (21.5 % w/w) on BMP values.

4. Conclusion

Based on the experimental results, we can draw the following conclusions.

1) When screenings are added to digested sludge, several beneficial properties are added to the hydrochar. These effects include: an increase in higher heating value (HHV), improved ability to remove water, a decrease in nitrogen (N) and sulphur (S) content, as well as a decrease in ash content and the following elements: alkali metals, alkaline earths, and heavy metals.
2) It has been observed that even though the co-HTC process has improved the quality of hydrochar, maximum value of screenings used is insufficient to enhance hydrochar to the quality of energy fuels (about 21–30 MJ/kg). However, higher quality hydrochar can replace dried sludge in incineration plant.
3) Co-HTC liquids have potential in biogas production, and its average BMP (except the liquid obtained from co-HTC thickened sludge with a screening content of 6.6 % w/w) are higher than the average values of HTC liquids from digested sludge.
4) It is important to note that co-HTC liquids tend to have extreme variations in BMP values for a given experiment, since the initial composition of screenings can vary greatly. If these liquids are directly digested, there is a risk of increased uptake of some by-products that interfere with AD processes.
5) The agricultural applications of hydrochar obtained at 200 °C are excluded due to the unreacted fractions of screenings in hydrochar. Increasing the process temperature to degrade the fractions would lead to an increase in the operating cost of the HTC system and an increase in potential inhibitors (refractory substances) in the HTC liquid limiting biogas production.

CRediT authorship contribution statement

Nina Kossińska: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Anna Grosser:** Writing – review & editing, Methodology, Investigation, Data curation. **Marzena Kwapińska:** Writing – review & editing, Resources, Methodology, Investigation, Data curation. **Witold Kwapiński:** Writing – review & editing, Resources, Methodology, Investigation, Data curation. **Heba Ghazal:** Writing – review & editing, Methodology, Formal analysis. **Hussam Jouhara:** Writing – review & editing, Supervision, Resources, Formal analysis. **Renata Krzyżyńska:** Writing – review & editing, Supervision, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2024.131456.

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