

A comparative study on biogas production, energy balance, and nutrients conversion with inter-stage hydrothermal treatment of sewage sludge

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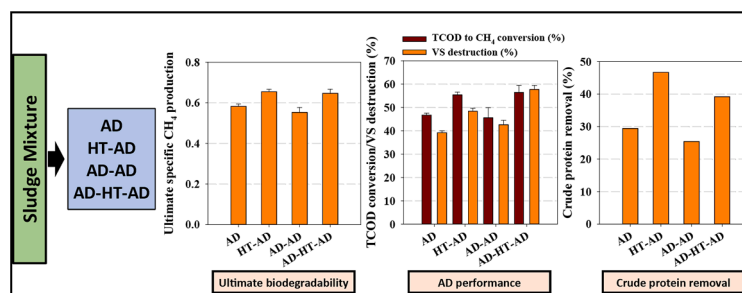
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HIGHLIGHTS

- One- and two-step anaerobic digestion resulted in comparable increase in methane production.
- Two-step anaerobic digestion led to higher organic matter but lower crude protein destruction.
- Two-step anaerobic digestion resulted in a lower soluble orthophosphate concentration.
- Heat recovery during hydrothermal treatment is required to obtain a positive energy balance.

GRAPHICAL ABSTRACT



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ABSTRACT

As an alternative to pre-stage hydrothermal treatment (HT) before anaerobic digestion (AD), inter-stage HT (i.e., AD-HT-AD) has been proposed to increase biogas production and to further reduce the residual organic matter. The goal of this study was to evaluate the effect of inter-stage HT at 155 °C on the ultimate biodegradability and AD extent of sewage sludge mixture (i.e., primary and waste activated sludge). The sludge ultimate biodegradability was evaluated through biochemical methane potential tests. AD-AD and AD-HT-AD configurations were investigated in semi-continuously fed bench-scale digesters in terms of methane production, solids reduction, nutrients transformation, and energy balance. Results were compared with those of AD and HT-AD configurations from our previous study. Inter-stage HT increased the ultimate biodegradability of the sludge mixture; however, pre- and inter-stage HT resulted in comparable overall specific methane production. Compared to AD and HT-AD, AD-AD and AD-HT-AD had comparable methane production, higher VS destruction (by 3.4–9.3%), but lower overall crude protein removal (by 4.0–7.5%) and soluble orthophosphate concentration decrease (by 32.5–60.8%). There was minimal difference in net energy production by AD and AD-AD (single digester vs. two digesters; 1.4 GJ/d), as well as by HT-AD and AD-HT-AD (pre-HT vs. inter-HT; 0.4 GJ/d). High HT heat recovery is needed for HT-AD and AD-HT-AD to obtain energy balance comparable to AD and AD-AD. Compared to single-step AD, the two-step AD process is more complex and thus less attractive for the digestion of sewage sludge with a relatively high ultimate biodegradability as was the case in this study. However, AD-HT-AD may be more beneficial considering post-AD sludge handling processes.

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1. Introduction

Large quantities of sewage sludge are generated in municipal water resource recovery facilities (WRRFs) globally. The combined annual production of sewage sludge in Europe, United States, and China has reached 240 million wet metric tons [1]. However, sludge must be treated before disposal or utilization to reduce its volume, and to minimize associated risks to the environment and public health [2]. However, due to its high organic content, sewage sludge has been regarded as a raw material for recovery of resources such as nitrogen (N), phosphorus (P), and bioenergy [3]. Anaerobic digestion (AD) of sewage sludge has been widely adopted for sludge stabilization, odor reduction, pathogen inactivation, organic matter destruction, and methane production [4]. AD has become an essential unit process in WRRFs due to its economical and environmentally friendly aspects [5]. However, sludge AD has a relatively low rate of biogas production, requiring long retention times to achieve a high extent of solids destruction [6].

Particulate matter hydrolysis is usually regarded as the rate-limiting step in the AD of sewage sludge [7]. Various treatment methods (mechanical, thermal, chemical, biological, and their combinations) have been explored to enhance organic waste solubilization and thus improve AD efficiency [8]. Among these methods, hydrothermal treatment (HT) results in high organic matter solubilization, pathogen inactivation, enhanced dewaterability, as well as increased solids reduction and biogas production in AD [9]. The effectiveness of HT is affected by HT temperature, duration, as well as sludge type and characteristics [10]. Pre-stage HT (i.e., HT-AD) has been widely tested at 60 to 270 °C to enhance the performance of AD with sewage sludge [11]. Pre-stage HT pretreatment time above a certain value, e.g., 24 h for 90 °C HTP and 90–120 min for 120–160 °C HTP [6] or 10 min for 170 °C HTP [12], did not result in additional sludge solubilization. In HT-AD, both complex compounds and readily biodegradable substances undergo HT before AD [13]. In addition, it has been reported that poorly degradable compounds associated with extracellular polymeric substances (EPS) are released during the AD of waste activated sludge (WAS) [14]. However, pre-stage HT cannot improve the conversion of the poorly degradable compounds released during AD.

As an alternative to pre-stage HT, HT can also be used as an inter-stage process (i.e., AD-HT-AD) to increase biogas production and to further reduce the residual organic matter [14]. In this configuration, as readily biodegradable substances have been degraded in the 1st AD, inter-stage HT targets the slowly biodegradable organic compounds in the sludge and those formed or released during the 1st AD. Compared to pre-stage HT, inter-stage HT can solubilize organic matter remained in the pre-digested sludge as well as EPS released during the 1st AD [15]. Indeed, one commercial HT technology, Exelys™ by Veolia, although initially proposed as pre-stage HT process, can also be placed between two digesters which is known as the Digestion- Lysis-Digestion (DLD) mode of operation [16]. Operational conditions of the Exelys™ continuous thermal hydrolysis system are 165 °C, 9 bar, and HT duration at least 30 min.

To date, a limited number of studies have compared the effectiveness of pre- and inter-stage HT on the performance of AD, with contradictory results reported. Several studies showed that, compared to HT-AD, AD-HT-AD led to higher methane production by 20% at 180 °C for 30 min [17], 9% at 130 °C and 29% at 170 °C for 15 min [18], and 22% at 120 °C for 1 h [19]. Yuan et al. [20] reported that pre- and inter-stage HT at 130–210 °C for 30 min resulted in comparable methane production by the AD of concentrated primary sludge (PS), while pre-stage HT was more energy efficient. Recently, Zhang et al. [21] reported that compared to the AD-HT-AD configuration, the overall methane production by HT-AD was higher by 4.7 to 7.6% with HT at 90 to 155 °C (3 h temperature ramping, 1 h at the target temperature). The differences among previous studies may be due to different sludge types used (WAS, PS, or PS and WAS mixture), HT temperature and duration, and

experimental AD mode (batch, semi-continuous, or continuous AD operation). Among the aforementioned seven studies in which the AD-HT-AD configuration was explored, four were conducted only in batch mode [14,18,20,21]. However, compared to batch assays, the results of continuously or semi-continuously fed digesters are more representative as their operational conditions reflect real AD applications [22]. Besides the AD-HT-AD configuration, other configurations involving inter-stage HT, such as AD-HT-pyrolysis [15] and AD-HT-centrate recirculation [23] have also been assessed. In the latter configuration, the digestate was hydrothermally treated at 160 °C for 30 min and then centrifuged; the centrate was returned to the anaerobic digester, whereas the sludge cake was disposed of [23]. Nuchdang et al. [24] tested a new configuration in which hydrothermal post-treatment was applied to algal solid digestate to maximize the release of organic compounds into the liquid phase, which was then recycled to the anaerobic digester to enhance AD.

In addition to biomethane, nitrogen (N) and phosphorus (P) recovery from sludge is another area of resource recovery with increasing interest. Typical N and P content of sewage sludge range from 1 to 8% and 0.5 to 5% (dry weight basis), respectively [25]. In the United States, ca. 60% of the sewage sludge is disposed of through land application [26]; thus, it is necessary to study the transformation of N and P during AD-AD and AD-HT-AD processes to understand their availability and thus decide on the best approach for their recovery from the treated sewage sludge. N in sludge exists as inorganic, mostly as ammonium N, and organic, such as proteins, amino acids, and other N-containing cellular polymers. Particulate organic N has to be solubilized in order to be recovered, for example during struvite crystallization [27]. HT and AD lead to organic N release and mineralization [28], which then can be recovered. Pre-stage HT at 90, 155, and 185 °C [29], as well as 125 and 225 °C [30], followed by AD led to the transformation of organic P to orthophosphate, which complexed with metal cations or other Al/Ca/Fe minerals resulting in decreased P availability. The transformation of P during AD-AD and AD-HT-AD has not been explored in semi-continuously fed digesters [31]. Besides, the transformation of heavy metals such as Cu, Zn, and Cr in sewage sludge during AD with pre- or interstage HT (i.e., HT-AD or AD-HT-AD, respectively) was explored in batch assays by Wang et al. [32]. Their study showed that similar reaction pathways occur in the HT-AD and AD-HT-AD configurations with some minor differences in metal species and content.

Among the above-mentioned five batch studies on AD-HT-AD, only the study by Yuan et al. [20], in which concentrated PS was used, provided comprehensive information on methane production, nutrients conversion, energy balance, and sludge dewaterability. Although Ortega-Martinez et al. [17] and Takashima [19] used both batch reactors and semi-continuously fed digesters with sewage sludge mixture, these studies did not cover nutrients conversion and energy balance. In summary, the AD-HT-AD configuration has not been comprehensively explored in terms of ultimate biodegradability of sewage sludge mixture (i.e., PS and WAS), as well as semi-continuous AD performance in terms of methane production and solids reduction, energy balance, and nutrients conversion.

In our previous study, conducted with sewage sludge mixture collected at the same WRRF as in the present study, the performance of AD and HT-AD was assessed in terms of sludge ultimate biodegradability, AD performance, energy balance, as well as N and P transformation [10]. Compared to only AD, pre-stage HT at 155 °C followed by semi-continuous AD resulted in higher methane production, solids reduction, overall crude protein removal, and organic N mineralization, but HT-AD decreased P availability. However, HT was energetically unfavorable and high HT energy recovery was required to achieve the same net energy gain as the control (i.e., AD only) [10].

The present study aimed to address the following questions: 1) To what extent would inter-stage HT lead to increase in the ultimate biodegradability of pre-digested sludge mixture? 2) Would inter-stage HT increase the methane production in semi-continuous digesters to such a level that results in a comparable or higher net energy gain

compared to AD only? 3) How is the N and P species distribution affected with inter-stage HT and AD, and what are the recommendations for effective N and P recovery? To accomplish the study goal, AD-AD and AD-HT-AD configurations with HT at 155 °C of sewage sludge mixture (i.e., PS and WAS) were assessed in terms of sludge ultimate biodegradability, AD performance, energy balance, as well as N and P conversion in bench-scale semi-continuously fed anaerobic digesters. Furthermore, data from the present study were compared to AD and HT-AD data from our previous study [10]. For a direct comparison of the data collected in the present study with those of our previous study which used AD and HT-AD, the sewage sludge mixture (i.e., PS and WAS) used in the current study was collected from the same WRRF. Sludge mixture was used in both studies as in most WRRFs PS and WAS or thickened WAS (TWAS) are combined before the sludge mixture is fed to the digesters, which is the case for the WRRF from which the sludge was obtained. To the best of our knowledge, there is no study on HT of sewage sludge mixture that assessed and compared all possible configurations (i.e., AD, AD-AD, HT-AD, and AD-HT-AD) using semi-continuously fed digesters, condition representing real municipal AD applications.

2. Materials and methods

2.1. Sludge mixture

Thickened sludge mixture of PS and WAS was collected at the F. Wayne Hill Water Resources Center (FWHWR Center; Buford, GA, USA), which uses enhanced biological P removal. Detailed operational conditions at the FWHWR Center for P release and recovery via struvite crystallization, as well as AD have been described in our previous study [10]. The collected sludge mixture was stored at 4 °C in the dark. Besides, anaerobic digestate collected at the FWHWR Center was used as inoculum for the biochemical methane potential (BMP) test and the startup of the bench-scale semi-continuously fed anaerobic digesters.

The characteristics of the raw sludge mixture, which is the same sludge used in our previous study [10] for AD at 20 d SRT, are shown in Table 1. The sludge was a mixture of 76/24% PS/WAS (TS basis) and had an ultimate biodegradability of $58.3 \pm 1.2\%$. However, the characteristics of the raw sludge mixture changed slightly over the storage time. The soluble chemical oxygen demand (SCOD) was higher than that of the previously used sludge [10] (14,170 vs. 10,720 mg/L), while other parameters were comparable. The volatile solids/total solids (VS/TS) ratio of the raw sludge mixture was 74.7%, whereas the total

chemical oxygen demand-to-volatile solids ratio (TCOD/VS) was 1.93. The TCOD-to-total N ratio (TCOD/TN) of the raw sludge mixture was 22.9. The TN/TS ratio and total P-to-total solids ratio (TP/TS) of the raw sludge mixture was 0.063 and 0.024, respectively, which are within the aforementioned literature reported N and P ranges. The soluble orthophosphate represented only 1.3% of TP.

2.2. Hydrothermal treatment (HT)

In our previous study [10], it was observed that pre-stage HT at 155 °C led to the highest increase in ultimate biodegradability and methane production, compared to the control (i.e., no HT treatment) and pre-stage HT at 90 and 125 °C. In order to compare data to those of our previous study [10], inter-stage HT at 155 °C was used in the current study. To evaluate the effect of inter-stage HT on the ultimate biodegradability and AD performance of pre-digested sludge (PDS; see Section 2.4 below), PDS was hydrothermally treated at 155 °C for 4 h as previously described [10]. Based on preliminary heating tests using our lab devices, it took 3 h to reach the target temperature; thus, the heating time was extended to 4 h (3 h temperature ramping and 1 h holding at the target temperature) [21]. The HT treated PDS (referred to as PDS-HT sludge) was stored at 4 °C in the dark until subsequently used in tasks described below.

2.3. Biochemical methane potential (BMP) test

The ultimate biodegradability of PDS and PDS-HT was evaluated through a BMP test at 35 °C using 580-mL glass aspirator bottles. Three batch reactors were set up, that is, seed blank, PDS, and PDS-HT. The liquid and headspace volume of each reactor was 400 and 180 mL, respectively. The batch reactors were set up by adding a certain sludge volume based on the sludge TCOD concentration for a target initial substrate concentration of ca. 3 g TCOD/L. The seed blank reactor did not receive any sludge. Then, 100 mL of medium [33] was added to each reactor. Inoculum (pre-incubated anaerobic digestate collected at the FWHWR Center) was anaerobically transferred to each reactor for an initial seed concentration of ca. 3 g TCOD/L. The reactors were incubated at 35 °C in the dark, continuously agitated with an orbital shaker (ca. 220 rpm). Biogas production and composition (CH₄ and CO₂) were measured regularly during the batch incubation. pH, SCOD, TCOD, TS, and VS were measured at the beginning and end of the incubation.

2.4. Semi-continuous AD operation

Two different configurations, that is, AD-AD and AD-HT-AD, were assessed in this study. First, one semi-continuously fed digester with 1-L working volume was set up for the 1st AD at 35 °C, operated for 87 days. The digester was fed every 2 days with raw sludge mixture, nominal SRT of 10 d and OLR of 7.0 g TCOD/L-d (equal to 3.6 g VS/L-d). The effluent (i.e., digestate, referred to as PDS) from the pre-digester was collected after day 30 (i.e., after three SRT values) and used later for the 2nd AD assessment. Half of the PDS was hydrothermally treated at 155 °C (referred to as PDS-HT) and used for the 2nd AD assessment. The characteristics of PDS and PDS-HT are presented in Table 1.

Two semi-continuously fed digesters using 2.8 L water-jacketed Spinner cell flasks (Bellco Glass, Inc., Vineland, NJ, USA) with a 0.75 L liquid, working volume were set up and operated at 35 °C for 36 d. The digesters were fed every 2 days, one with PDS and one with PDS-HT. It should be noted that preliminary feeding cycle measurements showed that the rate of methane production, thus the rate of sludge degradation, was relatively slow and constant over the 2-d feeding cycle. This is expected as most of the feed was particulate (raw sludge mixture, 81%; PDS, 94%; PDS-HT, 62%; see Table 1 for SCOD and TCOD values), which was utilized after slow hydrolysis. The nominal SRT and OLR for both digesters were 10 d and 3.0 g TCOD/L-d (equal to 1.8 g VS/L-d), respectively. In order to have the same OLR in all 2nd AD runs, both

Table 1

Characteristics of raw sludge mixture, pre-digested sludge (PDS), and pre-digested sludge hydrothermally treated at 155 °C (PDS-HT) used in this study.

Parameter	Raw sludge mixture (PS + WAS)	PDS ^b	PDS-HT ^c
pH	6.61	8.01	9.07
SCOD (mg/L)	14170 ± 290 ^a	2485 ± 35	16030 ± 90
TCOD (mg/L)	75940 ± 1493	39825 ± 163	41872 ± 123
TS (g/L)	52.5 ± 0.5	36.4 ± 0.1	38.5 ± 0.3
VS (g/L)	39.3 ± 0.3	23.8 ± 0.0	24.5 ± 0.2
VS/TS (%)	74.7	65.4	63.6
TCOD/VS	1.93	1.67	1.71
TN (mg N/L)	3310 ± 145	3036 ± 32	2949 ± 90
Ammonium N (mg N/L)	864 ± 12	1050 ± 36	1263 ± 13
Crude protein (mg/L)	15,288	12413 ± 301	10538 ± 569
TP (mg P/L)	1283 ± 52	1237 ± 19	1285 ± 78
Soluble orthophosphate (mg P/L)	16.1 ± 0.8	1.4 ± 0.1	2.3 ± 0.1

^a Mean ± standard deviation ($n = 3$).

^b PDS, pre-digested sludge mixture.

^c PDS-HT, pre-digested sludge mixture hydrothermally treated at 155 °C.

the PDS and PDS-HT were diluted to ca. 30 g TCOD/L and used as feed for the 2nd AD. The temperature of the digesters was maintained with heated water jackets connected to an external water heater/circulator. The digesters were continuously mixed with magnet-bearing, Teflon mixer assemblies (Bellco Glass Inc.), driven by external magnetic stirrers. The digesters were started with pre-digested anaerobic sludge collected at the FWHWR Center. Biogas produced by the pre-digester and the two 2nd AD digesters was recorded every day and every 2 days, respectively. Biogas composition (CH_4 and CO_2) and digestate pH were measured every 2 days. SCOD, TCOD, volatile fatty acids (VFAs), TS, VS, ammonium, and soluble orthophosphate were measured regularly. At the end of operation, the digestates were analyzed for pH, TS, VS, SCOD, TCOD, VFAs, ammonium, TN, soluble TN, TP, and soluble orthophosphate. All gas data reported here are at standard temperature and pressure (STP; 0 °C and 1 atm).

2.5. Analytical methods

pH, COD, TS, and VS were determined according to Standard Methods [34]. SCOD, ammonium, soluble TN, and soluble orthophosphate were measured in liquid samples after filtration through a 0.45 μm membrane. Ammonium was measured by the salicylate method (HACH Method 10031; HACH, Loveland, CO, USA). TN was measured by the persulfate digestion method (HACH Method 10208). TP and orthophosphate were measured by the molybdovanadate/acid persulfate digestion method (HACH Method 10127). Free ammonia (FA) was calculated as previously described based on measured total ammoniacal-N, pH and temperature [35]. Nitrite and nitrate were not detected in any sludge samples. Crude protein was estimated based on organic N (difference between TN and ammonium N), multiplied by a conversion factor of 6.25. Total gas produced was measured by displacement of an acidified brine solution (10% NaCl w/v and 2% H_2SO_4 v/v) in graduated columns equilibrated to atmospheric pressure. Biogas composition (CH_4 and CO_2) was measured by gas chromatography (GC) as previously reported [36]. VFAs were measured by high-performance liquid chromatography (HPLC) after the samples were passed through 0.2 μm PTFE membrane filters [37].

2.6. Data analysis

COD-based PDS solubilization after HT was calculated as previously described [10]. The AD rate and extent (P_u and k_f) of PDS and PDS-HT, reported as mean \pm standard error, were determined by non-linear regression using SigmaPlot (Version 14; Systat Software Inc., San Jose, CA, USA) based on the experimentally obtained methane production data (at 0 °C and 1 atm) during the BMP test assuming pseudo first-order kinetics for the overall digestion process (Eq. (1)) [33].

$$P_t = P_u[1 - \exp(-k_f t)] \quad (1)$$

where P_t is the seed blank corrected, specific methane production (SMP) at time t (g COD_M/g initial TCOD), P_u is the ultimate SMP (g COD_M/g initial TCOD), k_f is the pseudo first-order rate constant (d^{-1}), and t is the incubation time (d). COD_M is the COD equivalent of methane (350 mL CH_4/g COD converted at 0 °C and 1 atm).

2.7. Energy balance

Energy balance for the AD-AD and AD-HT-AD configurations was analyzed as previously described [10,38,39]. For the 1st AD and 2nd AD of the AD-AD and AD-HT-AD configurations, full-scale digesters were considered with a liquid volume of 1000 m^3 and a feed flow rate of 100 m^3/d , corresponding to 10-d SRT. Detailed assumptions, equations, and parameter values used for the energy balance calculations are presented in Text S1 and Table S1 (Supplementary Material). It was assumed that the 1st AD and the 2nd AD in the AD-AD and AD-HT-AD configurations

were conducted in sequence without any feed dilution. Thus, the OLRs of the 2nd AD with PDS and PDS-HT were 4.0 and 4.2 g COD/L-d based on TCOD concentration data shown in Table 1. As the actual, experimental OLR was ca. 3.0 g COD/L-d, the volumetric methane production used for the energy balance calculations was adjusted proportionally to the OLR of each AD.

3. Results and discussion

3.1. Effect of HT on PDS organic matter solubilization and VFA formation

The characteristics of PDS and PDS-HT are shown in Table 1. In agreement with previous studies [40,41,42], the COD-based solubilization of PDS by inter-stage HT at 155 °C increased significantly and reached 36.3%. In our previous study [10], which used the same raw sludge mixture, the COD-based solubilization was 37.9% after pre-stage HT at 155 °C.

During HT, VFAs are formed by oxidation of soluble organic compounds [43], carried out by free radicals in three steps: initiation, propagation, and termination [44]. The type and yield of VFAs by HT depends highly on the sludge characteristics and HT conditions, while the exact reaction pathways and kinetics are still unclear [10]. Fig. S1 shows the VFAs concentration and composition of PDS and PDS-HT. The total VFAs concentration of PDS and PDS-HT was 522 and 4514 mg COD/L, respectively. Thus, inter-stage HT significantly increased the VFAs concentration of PDS-HT. Acetate, n-butyrate, and n-valerate were the three major VFAs of the PDS. HT at 155 °C led to formation of acetate, propionate, i-valerate and n-valerate. In our previous study [10], the total VFAs concentration in the raw sludge mixture and pre-stage HT pretreated sludge was 6,339 and 12,001 mg COD/L, respectively. Pre-stage HT led to significant increase in n-butyrate and n-valerate concentration [10].

3.2. Ultimate sludge biodegradability

The BMP test lasted for 59 d. The pH in all series ranged from 7.24 to 8.01. Fig. S2 shows the cumulative total biogas, CH_4 , and CO_2 produced over the incubation period of the BMP test. Fig. 1 shows the seed blank corrected, specific methane production (i.e., methane-COD normalized to the initial TCOD). BMP test results are presented in Table S2. TCOD balance calculations for the BMP test series were performed by considering the initial and final measured substrate TCOD and methane-COD produced. Good COD balance was achieved for both BMP test series ($\leq 6.6\%$).

The seed blank corrected specific methane production data (Fig. 1) were used to fit the pseudo first-order kinetic model (Eq. (1)) (Fig. S3). The ultimate specific methane production (P_u) and pseudo first-order rate constant (k_f) (mean \pm standard error) were 0.211 ± 0.005 mg COD_M/mg COD and 0.067 ± 0.005 d^{-1} for PDS ($R^2 = 0.996$), and 0.378

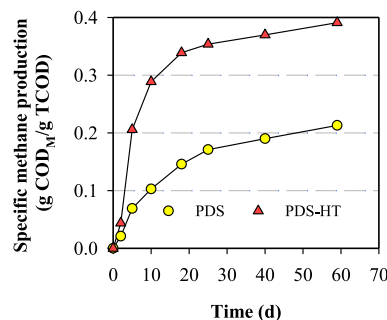


Fig. 1. Cumulative specific methane production (i.e., methane-COD produced normalized to the initial TCOD) for pre-digested sludge (PDS) and pre-digested sludge with hydrothermal treatment at 155 °C (PDS-HT). Batch incubation was carried out at 35 °C for 59 d.

± 0.014 mg COD_M/mg COD and 0.133 ± 0.017 d⁻¹ for PDS-HT ($R^2 = 0.982$). In our previous study [10], the P_u and k_f (mean \pm standard error) was 0.583 ± 0.012 mg COD_M/mg COD and 0.169 ± 0.016 d⁻¹ for raw sludge mixture ($R^2 = 0.985$), and 0.655 ± 0.012 mg COD_M/mg COD and 0.191 ± 0.017 d⁻¹ for pre-stage HT sludge at 155 °C ($R^2 = 0.986$). Thus, HT increased the ultimate specific methane production of both the raw sludge mixture and PDS. Compared to the raw sludge mixture, the effect of inter-stage HT was more pronounced for PDS. T-tests conducted based on the P_u and k_f estimated values resulted in the following conclusions: 1) pre- and inter-stage HT at 155 °C statistically significantly increased the P_u of raw sludge mixture and PDS ($p = 0.002$ and 0.003 , respectively); 2) pre-stage HT did not statistically significantly affect the k_f value of raw sludge mixture ($p = 0.178$); and 3) inter-stage HT statistically significantly increased the k_f value of PDS ($p \leq 0.001$).

Previously, Bougrier et al. [45] assessed the effect of pre-stage HT on five WAS samples with different ultimate biodegradability and reported a negative correlation between the increase in the extent of methane production after HT and AD and the ultimate biodegradability of the untreated WAS. In the present study, the raw sludge mixture had a high content of readily biodegradable organic substrates, as evidenced by the ultimate biodegradability of 58.3%. On the other hand, in the 1st AD, 43.3% of the TCOD in the raw sludge mixture was destructed (Section 3.3.1, below). As a result, PDS mainly contained hardly biodegradable organic substrates. Indeed, the ultimate biodegradability of PDS was only 21.1%, compared to 37.8% for PDS-HT. In a study by Ortega-Martinez et al. [17], the ultimate biodegradability of raw sewage sludge, pre-stage HT sewage sludge, digestate and inter-stage HT digestate was 57.9, 66.6, 13.5 and 38.0%, comparable to the values of the present study, except for that of digestate, which was lower.

3.3. Semi-continuous AD performance

3.3.1. First AD

The 1st AD to prepare pre-digested sludge used in AD-AD and AD-HT-AD was conducted in a 1-L semi-continuous digester fed with raw sludge mixture at 10 d SRT and a nominal OLR of 7.0 g TCOD/L-d. The operation lasted for 87 d, corresponding to 8.7 SRT values (Fig. S4). Performance data of the digester after day 30 (three SRT values) are presented in Table 2. The pH and SCOD were 7.65 ± 0.05 and $1,747 \pm 153$ mg/L, respectively. The ammonium and FA concentrations were $1,158 \pm 51$ and 70 ± 3 mg N/L, respectively. After day 30, the VFAs concentration was less than 130 mg COD/L, mainly acetate and n-valerate. A good TCOD balance during the 1st AD was achieved (2.8%;

Table 2).

In our previous study [10], a semi-continuous mesophilic digester fed with the same raw sludge mixture, operated at 20-d SRT achieved $46.7 \pm 0.8\%$ TCOD-to-CH₄ conversion and $39.2 \pm 0.8\%$ VS destruction. The TCOD-to-CH₄ conversion and VS destruction was ca. 3% lower in the present study ($43.3 \pm 3.0\%$ for TCOD, and $36.6 \pm 1.9\%$ for VS) (Table 2), due to a shorter AD SRT (10-d vs. 20-d). The small difference may result from the relatively high ultimate biodegradability of the raw sludge mixture ($58.3 \pm 1.2\%$). Wilson et al. [46] reported that mesophilic AD of sewage sludge mixture at 15- and 20-d SRT resulted in comparable VS destruction and biogas production.

3.3.2. Second AD

The 2nd AD assessment for the AD-AD and AD-HT-AD configurations was conducted in two 0.75-L semi-continuous digesters fed with PDS and PDS-HT, respectively, at 10 d SRT and a nominal OLR of 3.0 g TCOD/L-d. The operation lasted for 36 d, corresponding to 3.6 SRT values (Fig. S4). Performance data of the two digesters after day 30 (three SRT values) are presented in Table 2. The pH of the two digesters was 7.67 ± 0.02 and 7.57 ± 0.01 , respectively. Inter-stage HT enhanced both VS and TCOD destruction, as well as methane production. A good TCOD balance was achieved for both digesters (2.1%; Table 2).

HT resulted in higher SCOD and ammonium concentration (Table 2), attributed to the higher SCOD and ammonium concentration in the feed (Table 1). After day 30, the VFAs concentration in both digesters was less than 300 mg COD/L, indicating good performance with balanced acidogenic and methanogenic activity; acetate and propionate were the major VFAs, whereas acetate was predominant in the 2nd AD (AD-AD), and propionate was predominant in the 2nd AD (AD-HT-AD). The acetate and propionate fractions of total VFAs COD ranged from 84 to 93%, and 7% to 16% in the 2nd AD (AD-AD), and from 25 to 41%, and 59 to 75% in the 2nd AD (AD-HT-AD), respectively. The difference in VFAs composition may be attributed to the higher VFAs concentration in the feed to the 2nd AD (AD-HT-AD) (Fig. S1).

3.4. Pre- vs. inter-stage HT: Ultimate biodegradability and AD performance

For AD and HT-AD configurations, P_u was obtained in batch BMP tests. For AD-AD and AD-HT-AD configurations, the calculated overall extent of methane production considered both methane produced in the semi-continuous pre-digestion and in the batch BMP tests with PDS and PDS-HT. The P_u from the sludge mixture in the present study, as well as

Table 2

Performance summary of 1st AD and 2nd AD in the AD-AD and AD-HT-AD configurations. All AD reactors were operated with 10 d solids retention time, maintained at 35 °C.

Parameter	1st AD	2nd AD (AD-AD)	2nd AD (AD-HT-AD)
OLR (g TCOD/L-d)	6.99 ± 0.14^a	2.81 ± 0.01	2.88 ± 0.01
OLR (g VS/L-d)	3.62 ± 0.07	1.68 ± 0.00	1.68 ± 0.00
pH	7.65 ± 0.05	7.67 ± 0.02	7.57 ± 0.01
SCOD (mg/L)	1747 ± 153	1112 ± 84	3053 ± 13
Ammonium (mg N/L)	1158 ± 51	915 ± 28	1075 ± 36
FA (mg N/L)	70 ± 3	58 ± 2	55 ± 2
TS destruction (%)	26.3 ± 1.3	6.2 ± 0.9	23.5 ± 2.7
VS destruction (%)	36.6 ± 1.9	9.5 ± 1.2	33.3 ± 1.9
TCOD destruction (%)	43.3 ± 3.0	10.6 ± 2.7	28.8 ± 2.7
Biogas produced (mL/L-d at STP)	1365 ± 61	116 ± 9	372 ± 12
CH ₄ production (mL/L-d at STP)	991 ± 44	84 ± 7	269 ± 9
CH ₄ (%)	72.6 ± 1.5	73.0 ± 1.4	72.3 ± 0.6
Specific methane yield (mL/g VS _{added} at STP)	273 ± 12	38 ± 3	120 ± 4
TCOD-to-CH ₄ conversion (%)	40.5 ± 1.8	8.5 ± 0.7	26.7 ± 0.9
TCOD balance ^b (%)	2.8	2.1	2.1

^a Mean \pm standard deviation ($n \geq 3$).

^b TCOD balance (%) = $\frac{\text{TCOD}_{\text{influent}} - \text{TCOD}_{\text{effluent}} - \text{COD}_{\text{methane}}}{\text{TCOD}_{\text{influent}}} \times 100\%$.

Table 3

Overall methane production and solids destruction by four configurations. All AD reactors were operated with 10 d solids retention time, maintained at 35 °C.

Parameter	AD ^a	HT-AD ^a	AD-AD ^b	AD-HT-AD ^b
TCOD-to-CH ₄ conversion (%)	46.7 ± 0.8	55.4 ± 1.2	45.6 ± 4.3	56.4 ± 3.1
TS destruction (%)	28.1 ± 0.9	34.3 ± 1.1	30.9 ± 1.3	43.6 ± 2.2
VS destruction (%)	39.2 ± 0.8	48.4 ± 1.3	42.6 ± 1.9	57.7 ± 1.7

^a Data from Liu et al. [10].

^b Calculated based on data from Table 2.

that in our previous study [10] are as follows (in mg COD_M/mg COD): 0.583 ± 0.012 for AD, 0.655 ± 0.012 for HT-AD, 0.553 ± 0.024 for AD-AD, and 0.647 ± 0.020 for AD-HT-AD. The P_u values of AD and AD-AD, and of HT-AD and AD-HT-AD were very close. T-tests conducted based on the P_u values showed that there is not a statistically significant difference between the P_u of AD and AD-AD ($p = 0.125$), and between the P_u of HT-AD and AD-HT-AD ($p = 0.584$). Thus, pre- and inter-stage HT resulted in a comparable overall specific methane production from the sludge mixture. This conclusion agrees with that of a recent study which showed that HT as a pre- and an inter-stage process resulted in a similar increase of methane production from concentrated PS in mesophilic BMP tests [20].

AD, HT-AD, AD-AD, and AD-HT-AD configurations were compared in terms of methane production, as well as organic matter and solids destruction based on data of the present study, as well as from our previous study [10] (Table 3). Both pre- and inter-HT enhanced organic matter and solids destruction, as well as methane production. Compared to AD and HT-AD (single-step AD), AD-AD and AD-HT-AD (two-step AD) had comparable methane production, and higher VS destruction. T-tests based on data from Table 3 led to the following conclusions:

- 1) There was a statistically significant difference between the overall TCOD-to-CH₄ conversion in AD and HT-AD ($p \leq 0.001$), AD-AD and AD-HT-AD ($p = 0.024$); there was not a statistically significant difference between the TCOD-to-CH₄ conversion in AD and AD-AD, HT-AD and AD-HT-AD.
- 2) There was a statistically significant difference between the overall VS destruction in AD and HT-AD ($p \leq 0.001$), AD and AD-AD ($p = 0.046$), HT-AD and AD-HT-AD ($p = 0.002$), AD-AD and AD-HT-AD ($p \leq 0.001$).

Table 4

Energy components (GJ/d) for AD, AD-AD, HT-AD and AD-HT-AD configurations without or with 85% HT heat recovery. All AD reactors were operated with 10 d solids retention time, maintained at 35 °C.

Energy component	AD ^a	AD-AD	Without HT heat recovery		With 85% HT heat recovery	
			HT-AD ^a	AD-HT-AD	HT-AD ^a	AD-HT-AD
Input heat ($E_{i, heat}$)	5.5	5.4	55.6	55.6	55.6	55.6
Heat recovered ($E_{i, heat recovered}$)	NA ^b	NA	0.0	0.0	42.6	42.6
Heat losses ($E_{i, heatloss}$)	0.5	0.7	0.5	0.7	0.5	0.7
Input electricity ($E_{i, electricity}$)	0.8	1.0	0.8	1.0	0.8	1.0
Energy input (E_{input})	6.8	7.0	56.9	57.2	14.3	14.6
Energy output (E_{output})	37.0	35.8	43.8	44.5	43.8	44.5
Net energy gain (ΔE)	30.2	28.8	-13.1	-12.7	29.5	29.9

^a Data from Liu et al. [10].

^b NA, not applicable for control digester without HT.

Thus, although several studies reported that AD-HT-AD led to higher methane production than HT-AD [17,18,19], both BMP and semi-continuous AD operation data from the present study suggest that the two configurations result in comparable methane production, which is in agreement with the results of the study by Yuan et al. [20] in which concentrated PS was used. However, the beneficial effect of inter-stage HT is more likely greater than that of pre-stage HT for the AD of WAS in which poorly degradable compounds associated with EPS are released during AD [14,47]. The raw sludge mixture used in the present study had a high PS content (76%) and low WAS content (24%), which contributed to the relatively small difference in the extent of TCOD-to-CH₄ conversion between the HT-AD and AD-HT-AD configurations (Table 3).

3.5. Energy balance

The energy balance of AD-AD and AD-HT-AD configurations was calculated according to Equations S1-S7 (Text S1, Table S1) without and with HT heat recovery and experimental data from Table 2. Both 1st and 2nd AD data were considered. The results of the energy balance calculations are shown in Table 4. Detailed energy balance results for each process (1st AD, inter-stage HT, and 2nd AD) for the AD-AD and AD-HT-AD configurations are shown in Table S3. In the present study, 85% heat recovery was used in the energy balance calculations, which was previously assumed by Lu et al. [39] and also used in several other studies on the hydrothermal treatment of sewage sludge [20,38]. However, the measured heat recovery efficiency for sewage sludge has been reported as 72.8–78.5% [48]. For comparison, the energy balance results of AD and HT-AD configurations from our previous study [10] are also presented in Table 4. The net energy gain (ΔE) of AD-AD was slightly lower (by 1.5 GJ/d) than that of AD, due to slightly higher heat losses and electricity consumption (1.7 vs. 1.3 GJ/d), as well as lower energy output (35.8 vs. 37.0 GJ/d). Either without or with 85% HT heat recovery, the ΔE of AD-HT-AD was slightly higher (by 0.4 GJ/d) than that of HT-AD, due to higher energy output (44.5 vs. 43.8 GJ/d). Overall, there is minimal difference in the net energy production by AD and AD-AD (single digester vs. two digesters), as well as by HT-AD and AD-HT-AD (pre-stage HT vs. inter-stage HT). Both pre- and inter-stage HT had a negative effect on energy balance. High HT heat recovery (86% and 83%) is required for HT-AD and AD-HT-AD to obtain a net energy yield comparable to AD and AD-AD, respectively, which may not be possible to achieve.

The energy output is highly affected by the volumetric methane production rate, which in turn is affected by the VS content and ultimate biodegradability of the feed substrate [38]. In the study by Yuan et al. [20], with 85% HT heat recovery, the minimum VS content of concentrated PS to obtain a positive ΔE with pre- and inter-stage HT at 130 °C was 1.7 and 2.7%, respectively. Bjerg-Nielsen et al. [49] reported that the minimum feed VS content of pre-digested WAS to obtain a positive ΔE with inter-stage HT at 120 °C and 170 °C was 5.5 and 7.3%, respectively; 85% HT heat recovery was assumed. It should be noted that the above two studies were conducted using only batch BMP tests rather than semi-continuously fed digesters. As a result, the effect of SRT was either assumed by simulation [20] or ignored by considering only ultimate methane production [49]. Energy balance based on data obtained in the present study with semi-continuously fed digesters provides realistic, quantitative information for the scale-up and optimization of the combined HT and AD process for energy recovery from sewage sludge. In the present study, there is a slight difference between the energy balance and minimum VS content for AD and AD-AD, and for HT-AD and AD-HT-AD, due to comparable overall methane production (Table 3). With 85% HT heat recovery, the minimum VS content of raw sludge mixture to obtain a positive ΔE was estimated as 0.73% for AD, 0.79% for AD-AD, 1.17% for HT-AD, and 1.29% for AD-HT-AD. The actual VS content of the feed sludge mixture ranged from 3.4 to 3.8%, higher than the above-mentioned minimum

feed VS values to obtain a positive ΔE . Without HT heat recovery, the minimum substrate VS content to achieve a positive net energy yield was 4.48% for HT-AD and 4.64% for AD-HT-AD. Therefore, a positive ΔE was obtained for HT-AD and AD-HT-AD configurations with 85% HT heat recovery, whereas without HT heat recovery a negative ΔE was obtained for both configurations.

For the experimental setup of the current study and for a fixed SRT of 20 d, one way to increase the methane production rate and thus obtain a more positive energy balance is to increase the feed VS content by thickening. For HT-AD and AD-HT-AD to obtain a comparable energy balance to AD and AD-AD, the VS content of the sludge mixture has to be 7.1 and 7.0% without HT heat recovery or 4.1 and 3.9% with 75% HT heat recovery, respectively. Indeed, the VS content of the raw sludge mixture used in the present study was 3.93% (Table 1). Thus, practically, with 75% HT heat recovery, the HT-AD and AD-HT-AD configurations could obtain an energy balance similar to AD and AD-AD if the raw sludge mixture was fed directly to digesters without any dilution. Without or with lower HT heat recovery, the sewage sludge mixture has to be thickened to make the HT-AD and AD-HT-AD configurations more energy positive. However, energy for the thickening process should also be taken into consideration.

In summary, for the experimental setup and sludge mixture used in this study, inter-stage HT had a negative effect on energy balance. High HT heat recovery (83%) would be required for the AD-HT-AD configuration to achieve a net energy yield comparable to that of AD-AD. The energy balance of AD and AD-AD without HT, as well as HT-AD and AD-HT-AD with pre- or inter-stage HT, was comparable.

3.6. Transformation of N species

The distribution of N species in AD-AD and AD-HT-AD feed and digestate is shown in Fig. 2A. The TN in the raw sludge mixture consisted of 26.5% ammonium N, 13.9% soluble organic N, and 59.6% particulate N. The 1st AD increased the ammonium N and decreased the soluble organic and particulate N concentrations. The net ammonium N production during the 1st AD was 352 mg N/L. Inter-stage HT increased the

ammonium and soluble organic N, consistent with the effect of pre-stage HT assessed in our previous study [10]. The TN concentration in PDS and PDS-HT (Fig. 2A) was lower than that in the 1st AD effluent due to feed dilution for the 2nd AD as discussed in Section 2.4, above. The soluble TN-to-TN ratio of PDS-HT was 0.73, compared to 0.45 of PDS. Similar to the 1st AD, the 2nd AD resulted in a higher extent of organic N mineralization. The net ammonium N production was 173 and 208 mg N/L in the 2nd AD with PDS and PDS-HT, respectively.

Proteins are hydrolyzed during AD to peptides and free amino acids which are in turn oxidatively degraded to VFAs [50]. The crude protein concentration and distribution in the AD-AD and AD-HT-AD feed and digestate are depicted in Fig. 2B. The 1st AD at 10-d SRT led to 16.1% crude protein destruction. In our previous study [10], AD of the same raw sludge mixture at 20-d SRT resulted in 29.4% crude protein removal. Thus, as expected, crude protein removal increased with increased AD SRT for the same sludge.

Inter-stage HT led to crude protein destruction and solubilization. Solubilization was more pronounced than degradation, as evidenced by the lower ammonium N-to-soluble TN ratio of PDS-HT compared to PDS (0.59 vs. 0.77). These results are consistent with those of previous studies [6,10,12]. Indeed, it has been reported that high HT temperature (i.e., 300 °C) is generally required for protein degradation [51]. In the present study, inter-stage HT led to 15.1% PDS-HT crude protein destruction. In our previous study [10], pre-stage HT at 155 °C resulted in 24% crude protein destruction of the raw sludge mixture. Thus, the effect of HT on crude protein destruction was more pronounced with the raw sludge mixture than the PDS, a result of crude protein destruction in the 1st AD. The soluble crude protein in PDS and PDS-HT represents 15.9% and 52.8% of total crude protein, respectively. In our previous study [10], the soluble crude protein concentration in the raw sludge mixture and pre-stage HT sludge at 155 °C represented 6.3% and 62.6% of total crude protein, respectively.

The crude protein in the 2nd AD feed for the AD-AD configuration was lower than that in the 1st AD effluent due to 2nd AD feed dilution as discussed in Section 2.4, above. The 2nd AD led to a greater extent of crude protein destruction. The crude protein destruction was 10.6% and 14.2% by the 2nd AD in the AD-AD and AD-HT-AD configurations, respectively. Thus, inter-stage HT not only directly led to crude protein destruction (15.1%), but also increased crude protein destruction in the 2nd AD (by 3.6%). In our previous study [10], although pre-stage HT led to high crude protein destruction (24%), it did not increase crude protein destruction by AD. Indeed, there was minimal difference (<1%) in crude protein destruction by AD at 20 d SRT for the raw sludge mixture and pre-stage HT sludge at 155 °C [10].

Overall, AD-AD and AD-HT-AD led to 25.4% and 39.2% crude protein destruction, respectively. Thus, inter-stage HT significantly increased overall crude protein removal. In our previous study [10], the overall crude protein removal by AD and HT-AD with 20-d AD SRT was 29.4% and 46.7%, respectively. Thus, AD and HT-AD led to a higher extent of crude protein removal than the AD-AD and AD-HT-AD

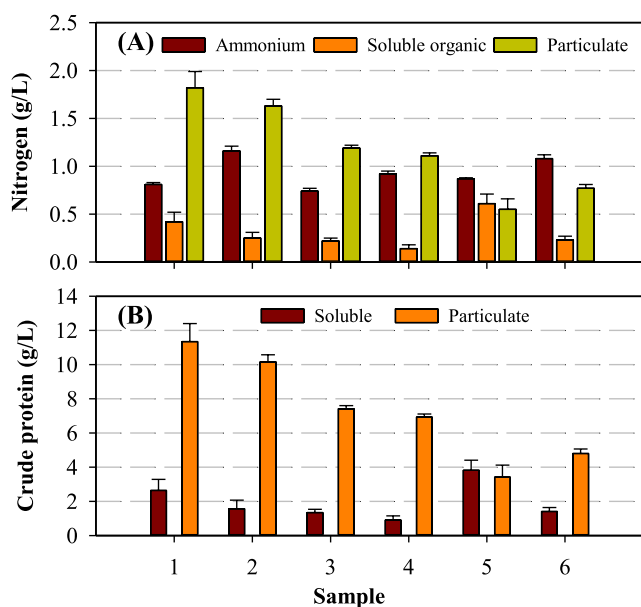


Fig. 2. Nitrogen species (A) and crude protein distribution (B) for AD-AD and AD-HT-AD feeds and effluents (i.e., digestates). Samples: 1, 1st AD feed; 2, 1st AD effluent; 3, 2nd AD feed (AD-AD); 4, 2nd AD effluent (AD-AD); 5, 2nd AD feed (AD-HT-AD); 6, 2nd AD effluent (AD-HT-AD). (Error bars are mean \pm standard deviation, $n \geq 3$). All AD reactors were operated with 10 d solids retention time, maintained at 35 °C.

Table 5

Influent and effluent TP and soluble orthophosphate, as well as TP balance for AD-AD and AD-HT-AD configurations. All AD reactors were operated with 10 d solids retention time, maintained at 35 °C.

Configuration	TP (mg P/L)		Soluble orthophosphate (mg P/L)		TP balance (%)
	Influent	Effluent	Influent	Effluent	
1st AD	1183 \pm 47 ^a	1245 \pm 21	14.8 \pm 0.7	3.2 \pm 0.2	−5.2
2nd AD (AD-AD)	874 \pm 13	907 \pm 18	1.0 \pm 0.1	5.0 \pm 0.3	−3.8
2nd AD (AD-HT-AD)	882 \pm 54	902 \pm 69	1.6 \pm 0.1	8.1 \pm 0.5	−2.3

^a Mean \pm standard deviation ($n \geq 3$).

configurations. For both the 1st and 2nd AD, very good TN balance was achieved (0.3–2.2%).

Based on the results of the present and our previous study [10], N recovery from sewage sludge after HT and AD is recommended, while pre-stage HT is preferable as it results in higher overall crude protein removal. Alternatively, protein recovery from hydrolysate after pre-stage HT, used as a raw material to make high added value products was proposed as another sludge valorization option [52].

3.7. P solubilization

Feed and effluent TP and soluble orthophosphate with the AD-AD and AD-HT-AD configurations are shown in Table 5. The soluble orthophosphate concentration in the raw sludge mixture was very low as the sludge at the WRRF undergoes P release before AD. Good P balance was achieved for all configurations ($\leq 5.2\%$). In the 1st AD, the soluble orthophosphate decreased by 78.3%. In our previous study [10], the soluble orthophosphate decreased by 87.5% after AD at 20-d SRT. Soluble orthophosphate decreases as the pH increases in AD [53]. In the present study, the pH of the raw sludge mixture was 6.61 (Table 1) and increased to 7.65 after the 1st AD (Table 2). As a result, the soluble orthophosphate decreased in the 1st AD. In the present study, inter-stage HT at 155 °C slightly increased the soluble orthophosphate of PDS-HT from 1.4 to 2.3 mg P/L (Table 1). The soluble orthophosphate in PDS (1.0 mg P/L) was lower than that in the 1st AD effluent (3.2 mg P/L), attributed to dilution of the 2nd AD feed, as well as pH change during storage of the PDS. Indeed, the pH of the 1st AD effluent was 7.65 ± 0.05 at 35 °C, which increased to 8.01 in the PDS after storage at 4 °C. Different from the 1st AD, the soluble orthophosphate in the 2nd AD with PDS and PDS-HT increased from 1.0 to 5.0 mg P/L, and from 1.6 to 8.1 mg P/L, respectively (Table 5). The pH of PDS and PDS-HT was 8.01 and 9.07 (Table 1), respectively, which decreased to 7.67 and 7.57 after 2nd AD (Table 2). Therefore, the soluble orthophosphate concentration decreased in the 1st AD, whereas increased in the 2nd AD. Considering both the 1st and 2nd AD in the AD-AD and AD-HT-AD configurations, the soluble orthophosphate decreased by 55.0 and 23.4%, respectively, which is lower than the decrease by AD (87.5%) and HT-AD (84.2%) observed in our previous study [10].

The speciation evolution of P in the solid phase of sewage sludge during both HT-AD and AD-HT-AD, investigated using batch AD assays, indicated that P cycling was strongly coupled with Fe chemistry [29,31]. For AD-HT-AD, the 1st AD induced formation of vivianite in the AD solids. Vivianite was further converted into strengite in the hydrochars derived from inter-stage HT at 155 and 185 °C, due to partial auto-oxidation by H₂O. Vivianite was formed again in the 2nd AD solids, resulting from microbial reduction of Fe(III) species [31]. Thus, both AD-AD and AD-HT-AD resulted in the transformation of complex P into orthophosphate, which was associated with Al/Ca/Fe minerals through adsorption and precipitation. Overall, the above reactions reduced P mobility and availability. The decrease in soluble orthophosphate after AD observed in the present study is consistent with the above-mentioned P speciation in the sludge after HT-AD and AD-HT-AD. Based on the results of the present and our previous study [10], P recovery from sewage sludge is recommended before HT and AD.

4. Conclusions

This study compared the ultimate biodegradability of a municipal sludge mixture and the performance of semi-continuously fed, bench-scale digesters operated at a SRT of 10 d for four configurations (AD, HT-AD, AD-AD, and AD-HT-AD). Pre- and inter-stage HT resulted in a comparable overall methane yield from the sludge mixture in batch tests. Results of semi-continuous AD operation showed that: 1) Single-step AD and two-step AD, as well as pre- and inter-stage HT resulted in comparable methane production; and 2) Compared to single-step AD, two-step AD led to higher VS destruction, but lower crude protein

destruction and a lower decrease in the soluble orthophosphate concentration. N and P recovery is recommended after and before HT and AD, respectively. There was minimal difference in the net energy production by AD and AD-AD (single digester vs. two digesters), as well as by HT-AD and AD-HT-AD (pre- vs. inter-stage HT). For the experimental setup and raw sludge mixture used in our previous and present study, significant recovery of HT heat is necessary to attain a net energy gain comparable to the control (i.e., AD without HT). Compared to single-step AD, the two-step AD process is more complex and thus less attractive. However, as two-step AD and inter-stage HT resulted in higher VS destruction, AD-HT-AD may be more beneficial considering post-AD sludge handling processes, such as dewatering, incineration, etc.

CRediT authorship contribution statement

Xiaoguang Liu: Methodology, Investigation, Writing - original draft. **Qian Wang:** Writing - review & editing. **Yuanzhi Tang:** Project administration, Funding acquisition, Writing - review & editing. **Spyros G. Pavlostathis:** Conceptualization, Methodology, Supervision, Writing - review & editing.

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.

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Declaration of Competing Interest

None.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apenergy.2021.116669>.

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