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Pilot-scale hydrolysis of primary sludge for production of easily degradable carbon to treat biological wastewater or produce biogas

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HIGHLIGHTS

- Hydrolysis of primary sludge produced 30–35 g volatile fatty acids/kg total solids.
- Optimal conditions for hydrolysis were 35 °C and pH 7.
- Hydrolysate centrate was as efficient as acetate in denitrifying treated wastewater.
- Hydrolysate centrate from a 100,000 PE plant could remove 235 kg N.
- Hydrolysate centrate as an alternative could produce 330 Nm^3 methane each day.

GRAPHICAL ABSTRACT
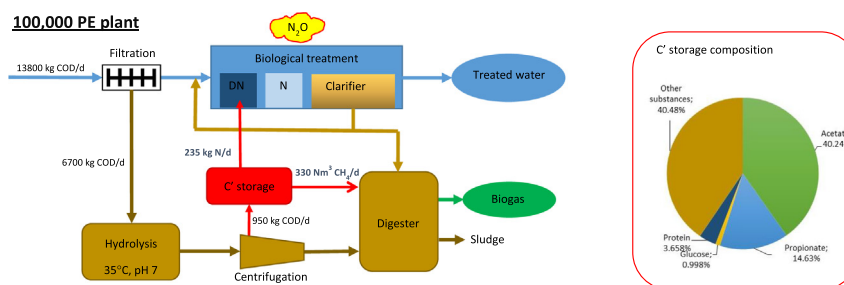
ARTICLE INFO

ABSTRACT

Organic compounds in wastewater are required for the biological removal of nitrogen, but they can also be used for biogas production. Distribution of the internal organic carbon at the plant is therefore critical to ensure high quality of the treated water, reduce greenhouse gas emissions, and optimize biogas production. We describe a wastewater treatment plant designed to focus equally on energy production, water quality, and reduced emissions of greenhouse gases. A disk filter was installed to remove as much carbon as possible during primary treatment. Primary sludge was then hydrolyzed and centrifuged. The hydrolysate centrate contained volatile fatty acids and was used either for the secondary wastewater treatment or to produce biogas. The yield during hydrolysis was 30–35 g volatile fatty acid per kg dry material or 40–65 g soluble COD per kg total solid. The specific denitrification rate was 20–40 g/(g·min), which is on the same order of magnitude as that for commonly used external carbon sources. Hydrolysis at around 35 °C and pH 7 gave the best results. The hydrolysate centrate can be stored and added to the biological treatment to improve water quality and reduce emissions of nitrous oxide or it can be used to produce biogas to optimize the operation of the plant.

1. Introduction

Wastewater contains large amounts of organic materials that can be used to produce energy (Kehrein et al., 2020; McCarty et al., 2011; Schopf et al., 2018). Plants in several countries works intensively to reduce the energy used to treat wastewater and increase the usable biogas produced from the resulting sludge. Replacing settling tanks with filtration units such as rotating belt sieves or disk filters have been done to remove more carbon during primary treatment and increase biogas production (Rusten et al., 2017). More advanced solutions have also been tested, including direct membrane filtration, adsorption, and dynamic sand filters (Hube et al., 2020; Sancho et al., 2019). Although not yet widespread among full-scale wastewater treatment plants, these methods have resulted in a net production of energy in some plants.

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Not all of the available carbon can be used to produce energy because some must be retained to remove nitrogen and phosphorus. Although phosphorus can be removed chemically, for example with iron or aluminum salts, nitrogen must be removed biologically because other methods such as stripping are too expensive. The carbon to nitrogen ratio (C/N ratio) required for biological processes has been calculated to 3.5–4.7 g COD per g N (Sobieszuk and Szewczyk, 2006). The anaerobic ammonium oxidation (anammox) process is a biological alternative for nitrogen removal that reduces the need for carbon, but the method is more complicated to control than conventional biological nitrogen removal (Winkler and Straka, 2019; You et al., 2020). Nevertheless, organic materials are required to remove or reduce the nitrogen in the treated water. If the C/N ratio is too low, an external carbon source must be added to ensure the quality of the effluent. This addition is expensive. It is more cost effective to use the carbon already present in the wastewater. Separating carbon during primary treatment therefore requires a balance between the goals of high-quality treated wastewater and optimal energy production.

The carbon footprint of wastewater treatment has received less attention than other costs or benefits. Carbon footprints are often measured in CO_2 equivalents and include the chemicals used, the transport of wastewater, the energy balance, and the emission of greenhouse gases such as nitrous oxide. Nitrous oxide is a greenhouse gas approximately 300 times as strong as carbon dioxide. It contributes approximately 40 % of the greenhouse gases resulting from wastewater treatment (Vangsgård and Madsen, 2020). Nitrous oxide is produced and released in aerated tanks during secondary treatment, and its emission increases when the C/N ratio is low (Kampschreur et al., 2009; Yan et al., 2017). If more carbon is removed during primary treatment, more nitrous oxide should therefore be produced and released. The amount of nitrous oxide produced is difficult to measure, but in a study of wastewater treatment plants in Denmark it varied from 0.24 % to 1.24 % nmol nitrous oxide per mol of nitrogen in the inlet, with an average emission of 0.84 % nmol nitrous oxide per mole N (Vangsgård and Madsen, 2020). Including greenhouse gas emissions during wastewater treatment may influence the plant's best use of internal carbon. In many countries including Denmark, energy becomes more climate friendly with its increased sustainable production from wind, solar, and water sources (Energinet, 2019). This reduces the positive effect of biogas production and may further affect the right balance between energy production, water treatment, and greenhouse gas emission.

In this study, a wastewater treatment plant has been designed with a minimized carbon footprint and a balanced focus on energy saving and production, water treatment, and greenhouse gas emissions. During primary treatment, as much carbon as possible will be removed and hydrolyzed to produce volatile fatty acids (VFA) from the primary sludge, which can be returned to the biological process for denitrification (Fang et al., 2020; Lin and Li, 2018; Liu et al., 2016; Liu et al., 2020). Higher pH levels increase the production of fatty acids (Chen et al., 2007; Zhou et al., 2021). Other parameters that influence the production of VFA include solid retention time, solid concentration, and type of sludge (Bouzas et al., 2002; Ucisik and Henze, 2008). The right balance between temperature, solid retention time, and pH during hydrolysis has yet to be found. The VFA produced will be separated from the solid materials e.g., by centrifugation. The hydrolysate centrate can then be used as an easily degradable carbon cocktail that can be stored and added to the biological treatment to improve water quality and reduce emissions of nitrous oxide or biogas production.

The objective of the study is to determine the optimal solid retention time, temperature, and pH during hydrolysis. The composition of the hydrolysate has been analyzed and as a novel part of the study, degradation of different organic compounds in the hydrolysate is followed during denitrification and used to evaluate the quality of the produced hydrolysate. The amount of N that can be denitrified by using the hydrolysate, has been calculated and compared with the amount of methane that can be produce from the hydrolysate. The innovative part of the study is the design of a wastewater treatment plant, where the hydrolysate can be directed either to the biological treatment or the digestor, and thereby ensure the optimal balance between water quality, emission of greenhouse gases and energy production.

2. Materials and methods

2.1. Sludge

Samples were collected from three different biological wastewater treatment plants (WWTPs): Bruunshåb, Mariagerfjord, and Aalborg West. All plants were in Denmark. Bruunshåb and Mariagerfjord WWTP were designed for 80,000 and 225,000 population equivalent (PE), respectively, but treat actual loads of 50,000 and 85,000 PE. Aalborg West WWTP were designed for 265,000 PE and equipped with enhanced biological phosphorus removal (EBPR). The plant treats actual loads of 198,000 PE. Laboratory scale experiments used primary sludge from Bruunshåb and Mariagerfjord WWTP. At Bruunshåb WWTP, samples were taken from the primary settling tank. At Mariagerfjord WWTP, the solid fraction of carbon was collected from incoming wastewater passed through a pilot-scale Hydrotech disk filter. Digested sludge was collected from Mariagerfjord and Bruunshåb WWTP and used in starting up the hydrolysis experiments. Activated sludge was collected from Aalborg West and used for the denitrification test. Samples were collected and laboratory experiments were done from April to June 2019. All samples were stored at 5 °C prior to use.

2.2. Hydrolysis experiment laboratory

Hydrolysis experiments were set up using 500 mL primary sludge spiked with 50 mL digested sludge in a 1 L Erlenmeyer flask. The Erlenmeyer flasks were placed in a shake incubator at constant temperature. Hydrolysis experiments were done at three different solid retention times (SRTs), 1, 2, and 3 days and at three different temperatures, 20 °C, 30 °C, and 35 °C. For experiments with SRTs of 1 or 2 days, primary sludge was added three times per day, and for experiments with an SRT of 3 days, primary sludge was added twice per day. Experiments continued for 19 days with pH measured every day and conductivity, soluble COD (sCOD), VFA, ammonium, phosphate, total solid (TS) content, and inorganic matter measured four times during the experiments and again at the end of the experiments. The Erlenmeyer flask was mixed gently before sampling. The hydrolyzed sludge from each plant was mixed and centrifuged at 1000g, 3000g, or 10,000g for 1, 3, or 10 min. The supernatant was decanted as hydrolysate centrate and analyzed by measuring the optic density at 600 nm (OD600) and the TS content.

2.3. Pilot-scale setup

A pilot-scale setup was installed at Mariagerfjord WWTP and test done in October 2022. Primary sludge was taken from the Hydrotech disk filter and continuously fed into a 3 m³ hydrolysis tank with a thermostat and a pH-regulator. Four experiments were done at pH values of 5, 6, or 7 and temperatures of 30 °C, 35 °C, and 40 °C. Without pH regulation, pH dropped to pH 5. For the experiments done at higher pH values, NaOH was added. The SRT was 3 days for all experiments. The hydrolysates were analyzed and separated by centrifugation. The hydrolysate centrate was analyzed by measuring ammonia, phosphate, sCOD, total COD (tCOD), VFA, pH, and conductivity. The specific denitrification rate was measured using the hydrolysate centrate as carbon source.

2.4. Specific denitrification rate

Sludge was collected from the biological tank (secondary treatment) at Aalborg West WWTP. The sample was heated to 23 °C, pH-adjusted to 7.5, and aerated with oxygen for 1 day. After this, 415 mL of the sludge was aerated with nitrogen for 10 min to remove dissolved oxygen. After 30 min, 2 mL 30.35 g/L $NaNO_3$ was added. Acetate or hydrolysate centrate was added to ensure a COD/N ratio of 6.2 which was expected to remove all nitrate (Sobieszuk and Szewczyk, 2006). Each experiment took 120 min and samples were taken after 2, 8, 14, 20, 40, 60, 80, 100, and 120 min

to measure nitrate, phosphate, COD, ammonia, and VFA content. The specific denitrification rate (SDNR) was calculated as

$$SDNR = -\frac{dC_N/dt}{TS}$$

where C_N is the concentration of nitrate (g N-NO$_3^-$/L) and TS is the concentration of dry material in the active sludge (g/L).

Phosphate concentration was measured during the experiment and used to calculate the P slip rate

$$P \text{ slip rate} = \frac{dC_P/dt}{TS}$$

where C_P is the concentration of phosphate (g P-PO$_4^{3-}$/L).

2.5. Analysis of sludge and hydrolysate

TS was measured by drying a 20 mL sample at 110 °C overnight and measuring the weight of the dried sample. The volatile solid was determined by measuring the loss on ignition at 550 °C at 2 h, and sCOD and tCOD were measured using the Hack Lange Kit (LCK 314). The ammonium concentration was determined using the Berthelot reaction (Searle, 1984). Salicylate was substituted for the toxic phenol. The total concentration of nitrogen was measured using the Hack Lange Kit (LCK 338). The total concentrations of phosphorus and ortho-phosphate were measured using standard methods (Eaton et al., 2005).

Ion chromatography was used to measure the concentration of VFA, which showed acetate and propionate as the most abundant. The concentrations of protein and humic acid compounds were determined using the modified Lowry method and measuring the reduction of Folin–Ciocalteau phenol with and without copper sulfate (Frølund et al., 1995). The concentration of saccharides was measured by treating the sample with H$_2$SO$_4$ in 100 °C for 14 min and then using a coloring reaction with anthrone (Raunkjær et al., 1994).

2.6. Plant calculations

Calculations were done for a reference wastewater treatment plant with a capacity of 100,000 PE, BOD 6000 kg/day, COD 13800 kg/day, and suspended solids (SS) 7400 kg/day (Supplementary materials). It was assumed that 70 % of the SS was removed during the primary treatment with the disk filter. The COD/N ratio was set to 4 kg COD/kg N both for the hydrolysate centrate and for external carbon, and the production of methane was set to 0.35 Nm^3 CH$_4$/kg COD assuming that 10 kWh can be produced per Nm^3 CH$_4$. It was assumed that 70 % of the COD produced in the hydrolysate could be used for denitrification. A mass balance was set up to calculate how much nitrogen and methane production could be removed by adding hydrolysate to the secondary treatment tank or the digestor. The cost of external COD was set to 0.61 Euro/kg COD and that of electricity to 0.15 Euro/kWh. Energy is required for pumping and separation. The energy consumption for the decanter centrifuge ranges from 1.3 to 8 kWh/m^3 (Szepessy and Thorwid, 2018). An extra tank has to be installed but hydrolysis is a part of the process for methane production (biogas) and implementation of the extra tank can be used as a method to increase the capacity of already existing plants.

3. Results and discussion

3.1. Laboratory hydrolysis experiments

Laboratory scale hydrolysis experiments were done using primary sludge from the full-scale primary settling tank at Bruunshåb WWTP. The TS was measured to be 51 % ± 3 % w/w and the pH as 5.96. Primary sludge from Mariagerfjord WWTP was taken from a pilot-scale disk filter unit, where the TS varied from 20 to 110 % w/w and the pH was 7.3. Experiments were set up with SRTs of 1, 2, and 3 days at 20 °C, 30 °C, and 35 °C.

pH was monitored during the 19 days of operation and decreased during the first 6 to 7 days, after which it was constant, as illustrated for the samples from Bruunshåb WWTP that was hydrolyzed at 20 °C (Fig. 1). At the end of the experiment at 20 °C, pH was measured to be 5.4 ± 0.4, and at 35 °C, pH was measured to be 5.0 ± 0.2. Notice that SRT barely affected the pH decline. Similar results were obtained in experiments done at higher temperatures and with primary sludge from Mariagerfjord WWTP, where steady state was also reached after 6 to 7 days. The pH decrease was due to the production of VFA. Gas formation was clearly observed as foam formation due to the microbial activity. Organic materials were degraded whereby CO$_2$ and H$_2$ were produced during hydrolysis and fermentation (Harirchi et al., 2022). Formation of air bubbles is required for foam formation as mixing was done gently. Actually bubble tests were often used to evaluate foaming propensity (Jiang et al., 2018). Foam is a serious operational problem in biogas plant and may be due to gas bubbles surrounded by liquid films and hydrophobic particles in the form of microorganism or suspended solids, but the process is still not well-understood (Yang et al., 2021; Boe et al., 2012).

The pH at steady state was lower for the experiments done at 30 °C and 35 °C than those done at 20 °C (Fig. 2).This is due to the higher degradation of solid materials at higher temperatures. Microbial activity increased with temperature, which is often described by using the Arrhenius relationship (Nottingham et al., 2019). At higher temperature, the death rate increase, so an optimum temperature exists. Several microorganisms are involved in VFA production (Harirchi et al., 2022), and previous study showed a decline in VFA production from 35 °C (mesophilic conditions) to 55 °C (thermophilic conditions) (He et al., 2012).

After hydrolysis, the dry matter content for primary sludge from Bruunshåb WWTP declined from 51 % ± 3 % w/w to 44 % ± 3 % (15 % decrease). The volatile solid concentration decreased from 44 % ± 4 % w/w to 38 % ± 2 % w/w (15 % decrease). Hydrolysis temperature and SRT seem to have only a minor influence on the final dry matter content. The dry matter content and the volatile solid concentration of the primary sludge from Mariagerfjord WWTP declined 14 % ± 8 % during the hydrolysis process.

Concentration of sCOD increases during hydrolysis (Table 1), whereby 10 % to 20 % of all CODs are solubilized after hydrolysis. Typical values from the literature range from 10 % to 30 % (Fang et al., 2020; Jørgensen, 1990; Karlson, 1990).

No clear trend was observed for temperature and SRT. The VFA concentration was measured as 1000 ± 400 mg/L. The relative concentration of VFA was measured as 10 to 30 mg VFA/g VS (Table 1). Hansen (2009) obtained 15 mg VFA/g volatile suspended solids (VSS) and Fang et al. (2020)
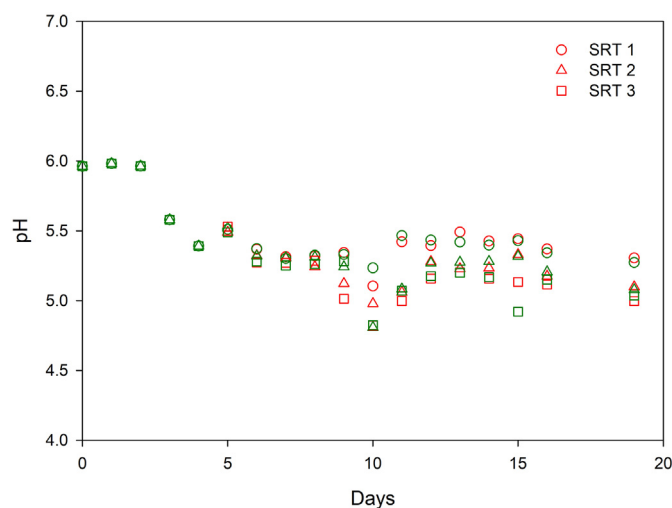

Fig. 1. Primary sludge from Bruunshåb WWTP, where pH development was followed in the hydrolysis tank with solid retention times of 1, 2, and 3 days at 20 °C. The two different colors represent two replicates.
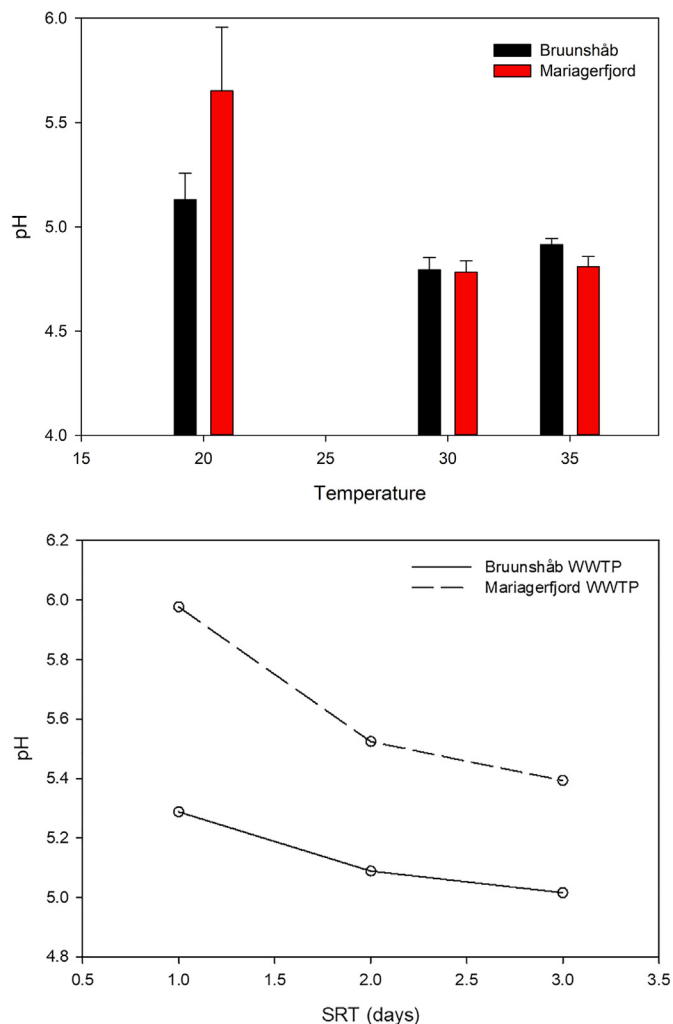
Fig. 3. Optic density (OD600) measured in the supernatant after centrifugation at 1000g, 3000g, and 10,000g for 1, 3, or 10 min.

could be removed at moderate rotation speed and centrifugation time. Not much difference was observed between hydrolysates from Bruunshåb or Mariagerfjord WWTP treated at the same centrifugation speed and time.

3.2. Pilot-scale test

A pilot-scale facility was installed at Mariagerfjord WWTP. Primary sludge was collected from a disk filter whereafter the primary sludge was hydrolyzed at various temperatures and pH levels, and at an SRT of 3 days. The dry matter content of the hydrolysate was measured to be 54 ± 1 g/L. The dry matter content of the supernatant after centrifugation (hydrolysate centrate) was measured as 3 to 9 g/L, i.e. 80 % to 95 % of the TS was removed during centrifugation. The dry matter content in the hydrolysate centrate was highest for the sample where the hydrolysis was done at high temperature and pH. Temperature increases microbial activity as already discussed. Furthermore, it is well-known that formation of VFAs reduces pH and thereby inhibits the microbial process (Jiang et al., 2013). Alkaline pH increases the solubility of organic materials, and thereby the bioavailability and production of VFAs (Cai et al., 2004) The concentration of sCOD varied between 2000 and 3500 mg/L and increased with the temperature during hydrolysis (Table 2). The concentration of VFA was measured as 900 to 1900 mg/L and increased with pH and temperature. It is thereby confirmed that temperature and pH are important for VFA production as observed in previous studies (Zhou et al., 2021; Lin and Li, 2018; Yuang et al., 2016). The concentration of VFA in the primary sludge was below the detection limit. The yield was measured as 30 to 35 g VFA per kg dry matter. Higher yield has been obtained at pH 9–10, but the required amount chemicals increase with higher pH (Liu et al., 2012; Wu et al., 2009).

The organic content of the hydrolysate centrates consisted of 50 to 76 % VFA, mainly consisting of acetate followed by propionate (Fig. 4). The

Fig. 2. Hydrolysate pH at steady state as function of temperature (A) or SRT (B).

obtained up to 300 mg/g VSS. Both the ammonia and orthophosphate concentrations increase in the liquid during hydrolysis; the ammonia concentration increased by 50 % to 180 % during hydrolysis. For orthophosphate, an increase of 50 % to 150 % was observed. During hydrolysis and fermentation, organic material was degraded, and ammonia and orthophosphate released to the liquid phase. Proteins are nitrogenous constitutes that are degraded to ammonium (Kayhanian, 1999). Both DNA and ATP contain phosphorus that are released as orthophospated during hydrolysis and fermentation. Further, polyphosphate accumulating organism (PAOs) release orthophosphate at anaerobic condition (Qiu et al., 2019).

Centrifuging the hydrolysate removed 85 % to 90 % of the TS from the hydrolysate centrate. Turbidity measured as optical density decreased as expected with rotation speed and time (Fig. 3). Still, most of the dry matter

Table 1
Sludge characteristics before and after hydrolysis.

	Bruunshåb WWTP		Mariagerfjord WWTP	
	Raw	Hydrolyzed	Raw	Hydrolyzed
sCOD/tCOD (%)	4.4 ± 0.3	14.4 ± 4.1	9.8 ± 7.5	17.4 ± 8.8
VFA/VS (mg/g)	0.4 ± 0.2	30.1 ± 12.6	0.3 ± 0.5	14.3 ± 4.4
P-PO$_4^{3-}$/VS (mg/g)	1.5 ± 0.3	3.3 ± 0.7	0.9 ± 0.6	2.3 ± 0.6
NH$_4^+$/VS (mg/g)	2.5 ± 0.3	5.2 ± 2.1	1.5 ± 0.8	2.3 ± 1.0

Notice: tCOD and sCOD is the total and soluble chemical oxygen demand, VFA is volatile fatty acids, and VS volatile solid. Average value and standard deviation is given in the table based on triplicates.
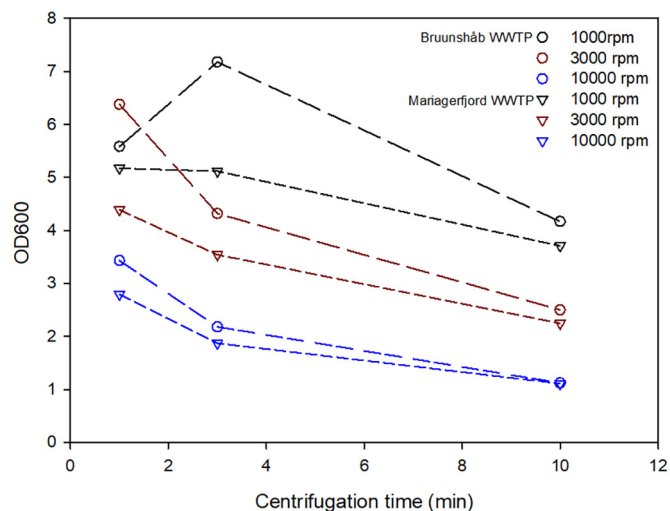
Table 2
Composition of hydrolysate before centrifugation.

	T 30 °C, pH 5	T 35 °C, pH 5	T 30 °C, pH 7	T 35 °C, pH 7
TS (%w/w)	0.74	0.35	0.85	0.88
Organic materials (%)	86	91	61	64
tCOD (mg/L)	13,266	6523	10,685	10,545
sCOD (mg/L)	2500	2100	2560	3430
VFA (mg/L)	929	1432	1619	1854
Yield (sCOD/tCOD) (%)	18	34	24	33
N-NH$_4^+$ (mg/L)	32	75	132	150
P-PO$_4^{3-}$ (mg/L)	16	41	57	31

Notice: tCOD and sCOD is the total and soluble chemical oxygen demand, VFA is volatile fatty acids, TS total solid.

T30 pH5

Acetate; 32.45%

Propionat...

Glucose; 0.741%

Protein; 0.125%

Other substance...

T35 pH5

Acetate; 33.61%

Glucose; 0.624%

Protein; 0.101%

Other substances; 22.17%

Propionate 43.49%

T30 pH7

Acetate; 49.20%

Propionate; 21.41%

Glucose; 1.395%

Protein; 3.571%

Other substances; 24.42%

T35 pH7

Acetate; 40.24%

Propionate; 14.63%

Glucose; 0.998%

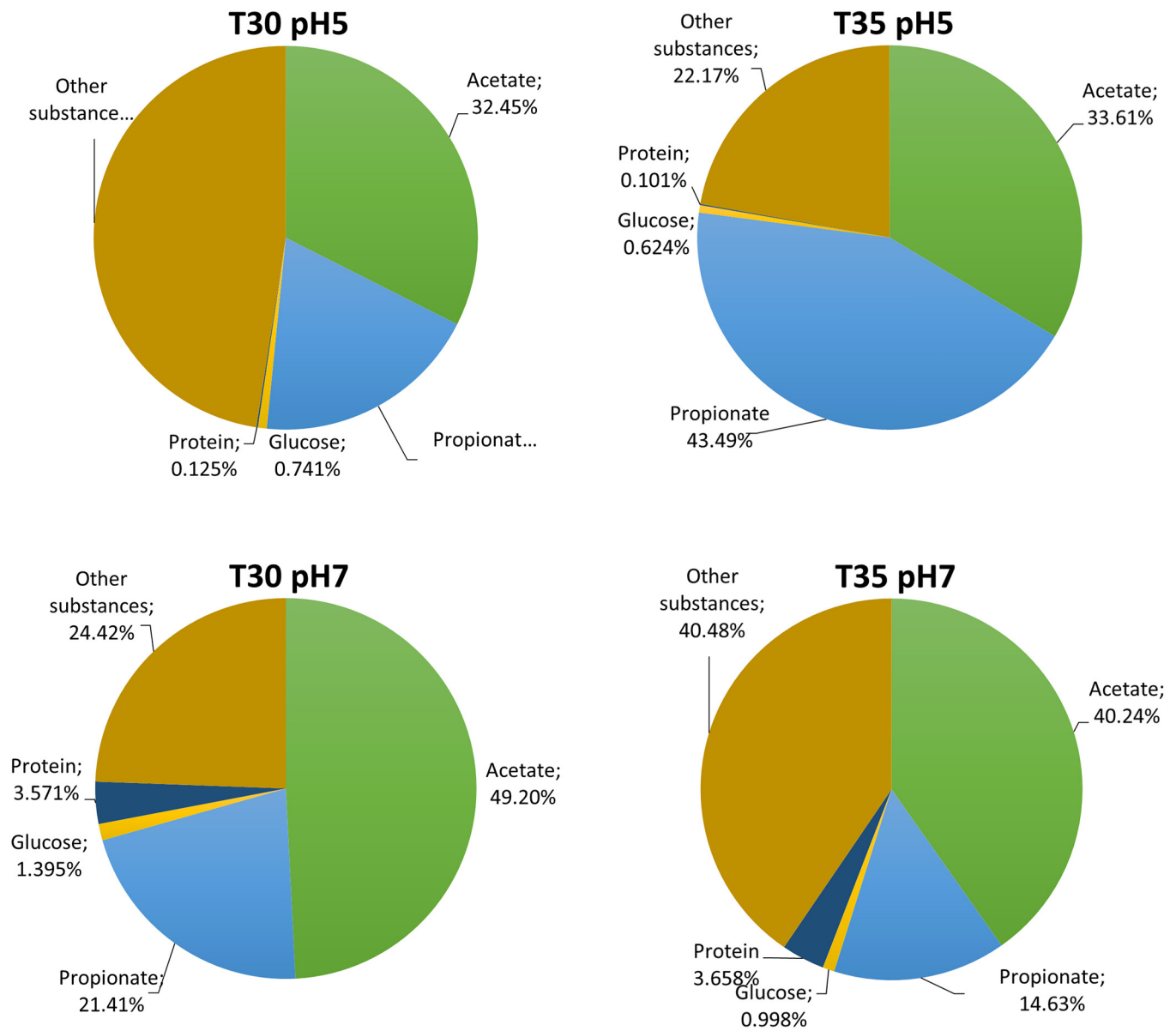Protein 3.658%

Other substances; 40.48%

Fig. 4. Analysis of sCOD in the centrates from the four hydrolysates. T30 indicates that the temperature during hydrolysis was 30 °C. Glucose includes all saccharides and polysaccharides.

relative acetate production increased with pH i.e., at pH 5 around 33 % of the soluble COD is acetate and at pH 7 40–50 % of the soluble COD is acetate. Acetate is produced in most hydrolysis studies of sludge and either propionate or butyrate are found in many studies, which corresponds well with the major pathways of anaerobic fermentation of sludge (Fang et al., 2020). Several microorganisms are involved in hydrolysis and fermentation. Some microorganism strains produce acetate, some propionic acids, and some butyric acid (Harirchi et al., 2022). There exist studies describing how the microbial community affects production of different VFA's (Harirchi et al., 2022). Proteins and saccharides contributed less than 5 % to the sCOD (Fig. 4). Proteins and saccharides may be released from the microorganism during hydrolysis. The residual fraction of sCOD has not been quantified. Ethanol is sometimes found in hydrolysate, but not in this study (Zhou et al., 2021).

The denitrification rate was measured by adding acetate or hydrolysate centrate to activated sludge. During the experiments, the concentration of nitrate decreased and was almost zero after 1 day (Fig. 5). The denitrification rate was calculated from the slope of the line for nitrate concentration as a

function of time. The phosphate concentration increased due to P stripping from the polyphosphate-accumulating organism (PAO) (Fig. 5). This shows that not all carbon was used for denitrification, but part of the carbon was used by the PAOs (Janssen et al., 2002). The concentration of phosphate declined again at the end of the experiment in the sample where acetate and hydrolysate produced at 30 °C was used. The concentration of ammonium was low and constant during the denitrification experiments (Fig. 5).

The concentration of VFA and other carbons are shown in Fig. 6. Propionate was consumed within 80 min in all experiments, and acetate within 100 to 120 min. Part of the residual carbon was degraded within the first 20 min, corresponding to a COD concentration of 60 to 80 mg/L. A fraction of the residual carbon was not consumed during the denitrification test. Despite that, the hydrolysate is an effective carbon source for denitrification due to VFAs. A carbon source is essential for the heterotrophic denitrification process (Fu et al., 2022). Low molecular weight organic compounds such as acetic acid and propionic acid are easy degradable, and the microbial yield are low (Hu et al., 2019). Furthermore, the nitrogen removal rate of acetic acid as an external carbon source is higher than of methanol
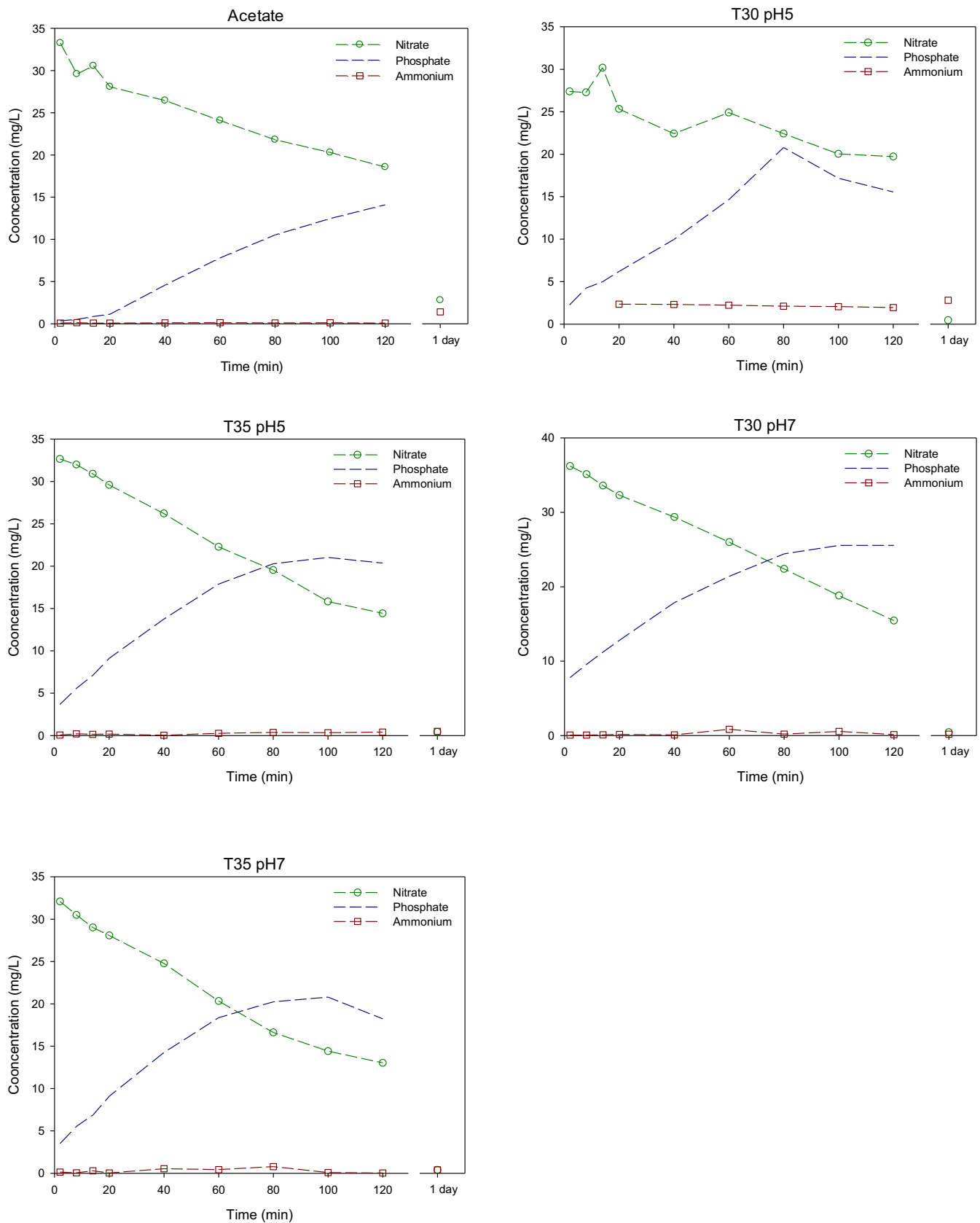
Fig. 5. Denitrification test where acetate or centrate from hydrolysate was used as carbon source.

and ethanol, as acetic acid can be used directly in the metabolic process (Chen et al., 2015). Thus, VFAs are ideal organic compounds as carbon source for denitrification (Hu et al., 2019, Fu et al., 2022).

The specific denitrification rate for acetate was measured as 30 g/g min (Table 3). Similar values have been observed in the hydrolysate (COD/N ratio around 6.2). Hydrolysates produced at high temperatures
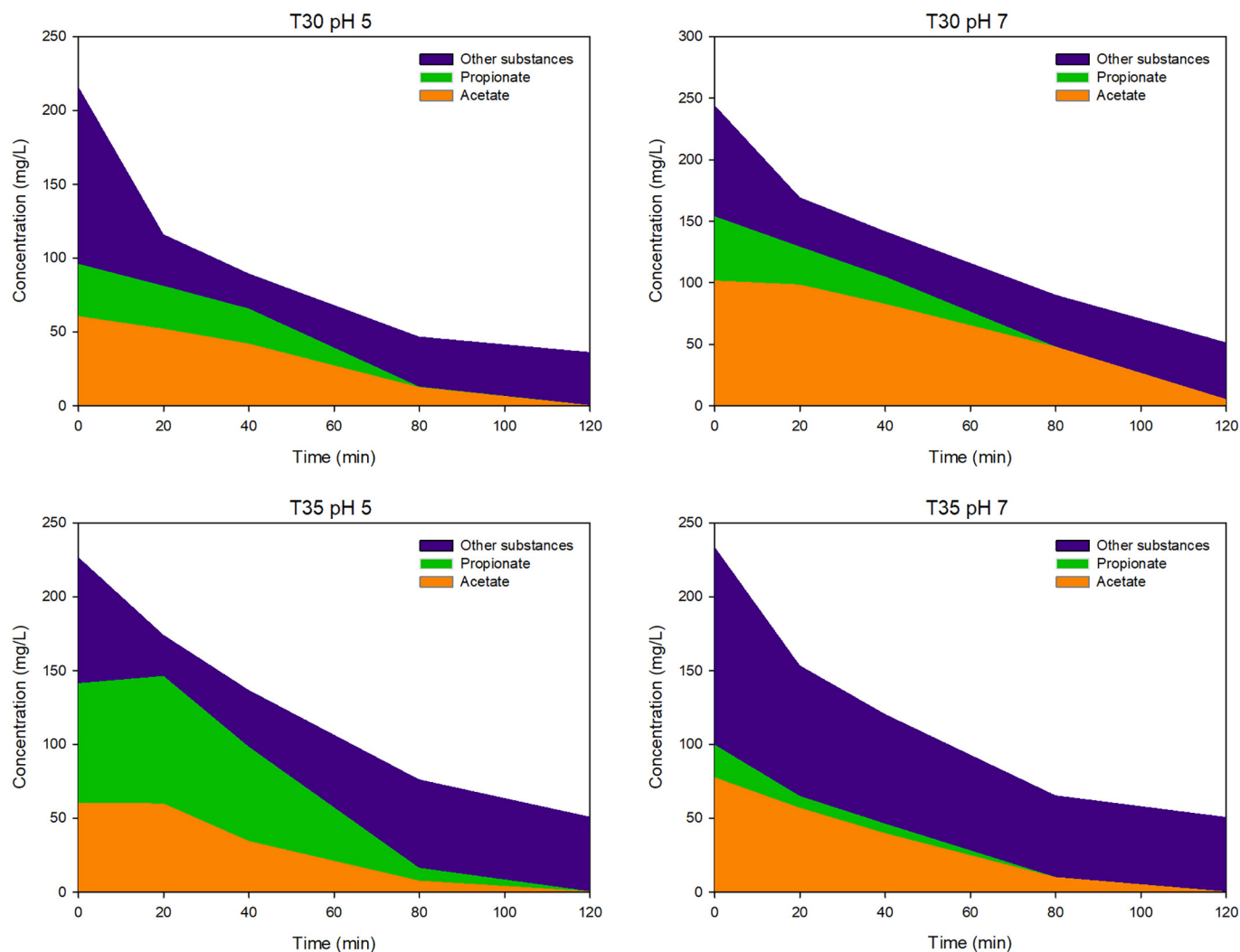
Fig. 6. Organic composition during denitrification test. Other substances were measured as sCOD minus propionate and acetate.

and pH levels reached a maximal SDNR of 45 g/g min (Table 3). The hydrolysate is a mixture of organic compounds including acetate and propionate at high concentrations and previous studies have shown that a mixture of organic compounds increase the denitrification rates (Liu et al., 2016). The reason may be that different denitrifies (microbes) uses different carbon sources, whereby a mixture of low-weight organic compounds may be beneficial for denitrification (Fu et al., 2022). A small amount of ammonium (2–4 g per kg VS) was released. These data are comparable with the results of other studies (Bouzas et al., 2002, Jônsson and Jansen, 2006).

Table 3

Specific denitrification rate and P slip rate after adding acetate or hydrolysate in a COD/N ratio of 6.2.

Compound	SDNR (g/g min)	P slip rate (g/g min)	$\Delta COD/\Delta N$
Acetate	30	33	6.5
Temp 30 °C and pH 5	23	38	6.7
Temp 35 °C and pH 5	43	44	6.9
Temp 30 °C and pH 7	46	47	6.7
Temp 35 °C and pH 7	42	49	7.1

Notice $\Delta COD/\Delta N$ is the consumption of COD measured per mg $N-NO_3$ removed. SDNR is the specific denitrification rate. This number also includes COD used for other purposes such as P stripping.

3.3. Plant calculations

An overall mass balance for a WWTP of 100,000 PE was set up, assuming that 70 % of SS are removed during primary treatment (Fig. 7). It was then possible to produce 1346 kg SS per day if 70 % of the produced COD was expected to end in the hydrolysate centrate (Supplementary materials). The rest of the sCOD was included in the wet solid fraction and therefore pumped to the digester. The hydrolysate centrate can be used in the biological tank to remove nitrogen or used in the digester.

The effect of the hydrolysis tank can be calculated in terms of how much external carbon can be saved. Assuming the same efficiency for the external carbon source as for the hydrolysate centrate, up to 940 kg COD external carbon can be saved per day. This will reduce the production of energy by up to 3300 kWh/day or 330 Nm^3 CH$_4$/day. Considering the cost of using external carbon and its lower production of energy or methane, costs can be reduced by using internal rather than external carbon. The savings of external carbon was estimated to 530 Euro/day, and 350 Euro/day if the number was corrected for the reduced methane production (Supplementary materials).

There are some extra set-up and operational costs associated with the extra tanks and process units. The cost and benefit of the process will be specific for the actual plant. In Fig. 8, three scenarios are shown. Scenario A is the reference, where all primary sludge is pumped directly to the digestor. Scenario B is a two-stage digestor which can be used to increase
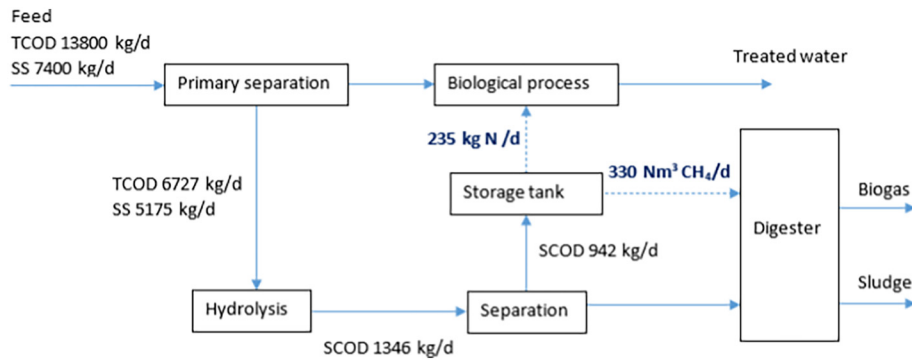
Fig. 7. Design parameters for wastewater treatment plant.

the capacity of an existing or to improve the methane production (Ghosh, 1991). Scenario C is the suggested solution, where a separation unit and storage tank has been included so it is possible to harvest the hydrolysate and use it either for denitrification or biogas production. The capital cost for scenario C has been estimated to 670,000–940,000 Euro, assuming that it is added to an already existing digestor (Scenario A), and the capacity of the existing digestor and biological treatment tank is sufficient. Production of hydrolysate can be used to improve the capacity of an existing digestor and biological tank, whereby other cost for expansions can be avoid.

Extra processes must be implemented including pumps and a separation unit e.g., a decanter centrifuge. Energy consumption of the decanter centrifuge is the most important and can vary between 150 and 1000 kWh/day. The electricity used for separation and pumps, and the reduced production of electricity from biogas sums up to 3800 kWh/day, if the energy consumption from pumps and separation is set to 500 kWh/day, and all hydrolysate is used for denitrification.

The suggested process (Scenario C) are relevant for WWTPs where the COD/N level is low and the carbon sources limited, or the nitrous oxide mission must be reduced. In Denmark this will include most of the largest WWTPs which include 30–40 plants (Miljøstyrelsen, 2020). The benefits are less consumption of external carbon, better use of the internal carbon, less emission of nitrous acids and higher capacity of the biological tanks due to the high denitrification rate. The hydrolysate can thereby be used as a method to boost denitrification. The establishment costs are thereby calculated to be up to 940,000 Euro and the yearly savings up to 97,000 Euro/year. These numbers may vary from plant to plant. Overall calculations can also be found elsewhere (Miljøstyrelsen, 2020).
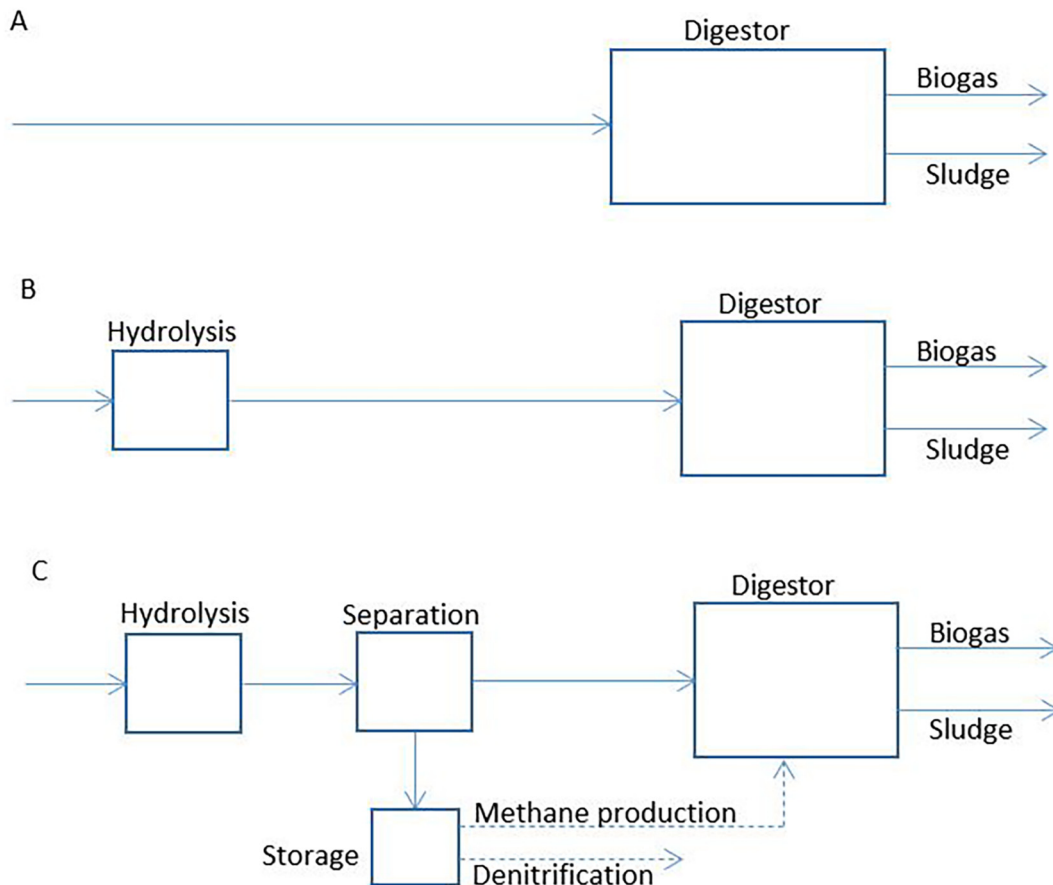

Fig. 8. Alternative routes for primary sludge A) digestor, B) two-stage solution with hydrolysis and digestor, and C) hydrolysate for biological treatment or biogas production.

The system is flexible, so it is possible to prioritize low N$_2$O emission and high water quality or biogas production by increasing or decreasing the flow of hydrolysate centrate during the biological process. Flexibility is further improved by use of the storage tank.

4. Conclusion

Hydrolysate was produced from primary sludge to produce a liquid cocktail with VFA that was stored and used either for secondary treatment of wastewater or for biogas production. Hydrolysis at temperatures around 35 °C and pH 7 gave the best result, but adjustment was required to keep the pH at 7. Without pH adjustment, pH drops to 5–5.5. Thus NaOH must be added to keep pH at 7 during hydrolysis. The yield during hydrolysis was measured as 30 to 35 g VFA/kg TS or 40 to 65 g sCOD/kg TS. The primary VFAs produced was acetate and propionate. Besides VFAs, the sCOD also consist of a minor fraction of saccharides and proteins. Residual sCOD have not been identified and was not degraded during denitrification. The specific denitrification rate was measured as 20 to 40 g/g min, similar to values found for commonly used external carbon sources. Both acetate and propionate were degraded during denitrification. Data from the experiment was used to design a climate-friendly WWTP. For a 100,000 PE WWTP, it will be possible to produce approximately 950 kg sCOD per day and thereby remove 235 kg N. If carbon is not necessary for the biological treatment, 330 Nm^3 methane can be produced from the hydrolysate. Installation of a hydrolysis tank, separation unit and storage tank will thereby give a flexible plant where the primary sludge can be used either for water treatment or gas production.

Abbreviations

C/N ratio	Carbon to nitrogen ratio
COD	Chemical oxygen demand
EBPR	Enhanced biological phosphorus removal
P slip rate	Phosphorus slip rate
PAO	Polyphosphate-accumulating organism
PE	Population equivalent
sCOD	Dissolved COD
SDNR	Specific denitrification rate
SRT	Solid retention time
SS	Suspended solids
tCOD	Total COD
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

CRediT authorship contribution statement

M.D.J., K.S. and M.L.C. got the idea and formulated the overall research goal and aim. A.H.J., C.K.H., M.S., R.B.M.A. planned and carried out the experiments, and analyzed the data. A.H.J., C.K.H., M.S., R.B.M.A., and M.L.C. worked out almost all of the technical details, and performed the numerical calculations for the suggested experiment. K.S. performed the mass balance for a full plant. M.L.C. took the lead in writing the manuscript and was responsible for supervision. All authors provided critical feedback and helped shape the research, analysis, and manuscript.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.157532.

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