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Review

Impact of process parameters of thermal alkaline pretreatment on biogas yield and dewaterability of waste activated sludge

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ABSTRACT

Thermal alkaline pretreatment (TAP) of waste activated sludge (WAS) before anaerobic digestion (AD) was reviewed. Focus of the review was on impact of TAP process parameters on biomethane yield (BY) and kinetics of AD and downstream dewatering. With higher initial biodegradability of untreated WAS, effect of TAP on BY decreases. Depending on initial biodegradability, BY increase of 22–97% is expected. Treatment temperatures below 100 °C showed to be as effective as temperatures higher than 100 °C in terms of BY increase. Alkali dosage and resulting initial pH have a significant effect on BY increase and showed to have an optimum range of 40–60 mg NaOH per g total solids (TS) of sludge. It is advised that alkali is dosed based on solids content in WAS and monitored by pH. Treatment time of 1.5–5 h is sufficient for an effective low temperature TAP ($T < 100$ °C), with longer treatment times showing no positive impact on BY increase. Load of sludge liquor with organics and nutrients increases with more intensive TAP conditions. Despite kinetic enhancement of hydrolysis step in AD, more research is needed to clarify if TAP improves kinetics of entire AD process which determines required digester volume. Impact of TAP on dewaterability of digestate is ambiguous and needs more investigation using standardized methods, also with regards to potential effects on polymer demand. Findings of experimental studies were reflected against available data from commercialized TAP process of Pondus®, throughout review. Finally, important process design parameters of TAP such as input TS and point of alkali dosage are discussed and recommendations for future research are presented.

1. Introduction

Waste activated sludge (WAS) is the unfavorable byproduct of sewage treatment process, which accounts for up to 50% of treatment costs on a wastewater treatment plant (WWTP) (Appels et al., 2008). Therefore, its reduction can lead to significant savings in disposal costs. Fresh WAS from clarifiers typically consists of around 99% water and 1% solids (organic and inorganic). To reduce sludge handling costs, it is favorable to reduce these three parts (water, organic and inorganic solids) as much as possible in most economical ways. Thickening and dewatering units in a WWTP are responsible for reduction in water content. Anaerobic digestion (AD) turns part of organic matter in WAS into biogas, which leads to renewable energy production and sludge solids reduction, simultaneously. The inorganic solids in WAS are mostly untouched and remain in final dewatered sludge and must be disposed.

Due to limited and kinetically slow organic solids reduction of WAS in AD (30–45%) and its poor dewatering potential (typically not more than 15–20% total solids (TS) can be reached), pretreatment techniques have been broadly investigated in the last decades to improve both aspects (Carrere et al., 2010; DWA, 2008, 2014). They include mechanical and non-mechanical (thermal, chemical, physical, and biological) techniques or a combination of these which primarily target the low and slowly biodegradable structure of WAS leading to solubilization of solids and release of organic matter into the liquid phase. This consequently accelerates the rate limiting hydrolysis stage of AD and potentially increases biogas yield. These techniques differ in efficiency, effects, complexity, costs of operation, etc. Among all, thermal pretreatments have gained much interest in terms of full-scale installations, due to their proven effects and energy integration potentials on a WWTP. High temperature thermal pretreatment ($T \sim 170$ °C) known as thermal hydrolysis (TH) has proven many advantages regarding sludge viscosity reduction, organic loading rate increase in AD, biogas yield increase,

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solids reduction, and dewatering improvements (Barber, 2016). As an alternative to TH, thermal alkaline pretreatment (TAP) is a combined technique which exploits potentials of both thermal and alkaline pretreatments, together. It has been tested in high ($T > 100$ °C) as well as low ($T < 100$ °C) temperature ranges. However, high temperature TAP is subject to unfavorable issues associated with high temperatures plus their adverse combined effects with alkali addition (Delgenès et al., 2000; Penaud et al., 1999; Penaud et al., 2000; Stuckey and McCarty, 1984). On the contrary, low temperature TAP has gathered much more attention due to its simpler operating conditions and less intensive drawbacks (DWA, 2016). Advantages and disadvantages of low temperature TAP before AD are listed in Table 1. Moreover, Table 2 summarizes a brief comparison of low temperature TAP with high temperature TH. Process flow schematic of sludge treatment line including TAP before AD is shown in Fig. 1. Primary sludge (PS) has inherently better dewatering potential and higher anaerobic biodegradability than WAS. Therefore, it is more meaningful to leave PS out of pretreatment and use it for cooling and neutralizing pretreated WAS, instead.

TAP of sewage sludge has been extensively studied in last decades in experimental studies, and research interest has increased significantly during recent years (Figure S1). Nevertheless, there was no comprehensive literature review on this potential technique. Reported studies from literature apply various methods for TAP trials, use different process conditions, and investigate the process parameters using different methods for analytics and measurement. In addition, sludge quality as important input material differs from study to study. This diversity makes it very difficult to compare results of different studies to each other and validate or cross-check future findings between individual studies. Therefore, the aim of this review was to extract, summarize, analyze, and interpret the results of studies in literature to report on current knowledge and identify topics for future research. The focus of this review is on effects of TAP process parameters on AD regarding biomethane yield (BY) increase, composition of biogas and kinetics of biomethane production. Subsequently, effects of TAP on digestate dewaterability and sludge liquor quality as two important economic factors are discussed. For all parameters, findings of experimental studies are reflected against available data from full-scale installations of TAP based on the Pondus® process. This commercially available TAP process has been installed in several full-scale WWTPs and is operated with specific process conditions (specifications in Table 3, process configuration in Fig. 1). Finally, important TAP process design parameters are discussed and recommendations for future research are presented.

Table 1
Advantages and disadvantages of low temperature thermal alkaline pretreatment before anaerobic digestion.

Advantages	References
Significant solubilization of particulate organic matter (proteins and carbohydrates) leading to increased kinetics of hydrolysis step of AD.	(Campo et al., 2018; Liu et al., 2019; Zawieja, 2019)
Significant viscosity decrease facilitating pumping and mixing leading to better mass transfer and kinetics enhancement of AD.	(Li et al., 2017b; Ruiz-Hernando et al., 2014; Wang et al., 2016b)
Biogas yield increase and subsequently less organic solids to dispose.	(Campo et al., 2018; Heo et al., 2003; Nagler et al., 2016; Ruffino et al., 2016)
Potential of foaming suppression in digester.	–
Potential of hygienization (when primary sludge (PS) is also hydrolyzed).	–
Disadvantages	References
Return load increase (particulates and soluble organics and nutrients) leading to more capacity and costs needed to re-treat sludge liquors in main- or side-stream.	(Guo et al., 2017; Park et al., 2014; Toutian et al., 2020a)

Table 2
Comparison of low temperature thermal alkaline pretreatment (TAP) with high temperature thermal hydrolysis (TH).

Parameter	TH ($T \sim 170$ °C)[a]	TAP ($T < 100$ °C)[b]
Pre-dewatering before pretreatment	Requires pre-dewatering to 16–18% to be energy efficient (higher polymer demand)	Suffices thickening to 6–8% (lower polymer demand)
Heat demand	High heat demand	Low heat demand
Energy source	Requires boiler to produce high temperature steam or hot oil	Does not require a boiler, works well with hot water from a combined heat and power plant (CHP)
Viscosity reduction	Significant	Significant
Digestion capacity increase	Increase of digestion capacity up to two times due to viscosity reduction and pre-dewatering of WAS plus possible capacity increase due to kinetics enhancement of AD	Possible capacity increase due to kinetics enhancement of AD
Biogas yield increase and organic solids reduction	Potential increase in biogas leading to decrease in organic solids	Potential increase in biogas leading to decrease in organic solids
Digestate dewatering and polymer demand	Increases dewaterability with increase in polymer demand	Needs more research (to be discussed in Section 3)
Sludge liquor quality	Increase in loads of organics and nutrients	Increase in loads of organics and nutrients
Complexity of operation	More complex (high temperature and pressure handling)	Less complex (highly concentrated alkali handling)
Flexibility	Requires stable performance of pre-dewatering equipment in delivering sludge with 16–18% TS	No specific complexities leading to flexibility complications
Capital costs	Requires higher capital costs due to multi-stage reactors, robust construction material and complex controlling system needed for high pressure and high temperature conditions, off gases handling, (or clean in place for processes with thermal oil heat exchanger)	Less capital costs due to simpler construction material and controlling system owing to ambient pressure and low temperature conditions, no off-gas handling
Operational costs	Requires skilled operating staff, extra fuel to produce required steam	Does not require skilled operating staff, requires permanent supply of alkali
Full scale installations	More than 70 since 1995	Less than 10 since 2004
Well known suppliers (heating medium)	Cambi (vapor), Veolia (vapor), Sustec (vapor), Haarslev (vapor), ELIQUO STULZ (hot oil)	Pondus® (hot water), Lystek

[a] references: Barber (2016), DWA (2016), operational manuals.
[b] references: DWA (2016), operational manuals.

2. Anaerobic digestion

2.1. Biomethane yield increase

In this section, effect of initial biodegradability of sludge on BY increase is clarified, first. Afterwards, to determine the effect of different ranges of temperature, alkali dosage and treatment time on BY increase and consequently finding optimum conditions, absolute BY increase is used as the target parameter. During collection of data, it was noticed that researchers use different test methods and various units to report biogas production data. This makes collection and interpretation of data challenging, while there are already standardized test methods for biomethane potential measurement. Accordingly, it is highly recommended

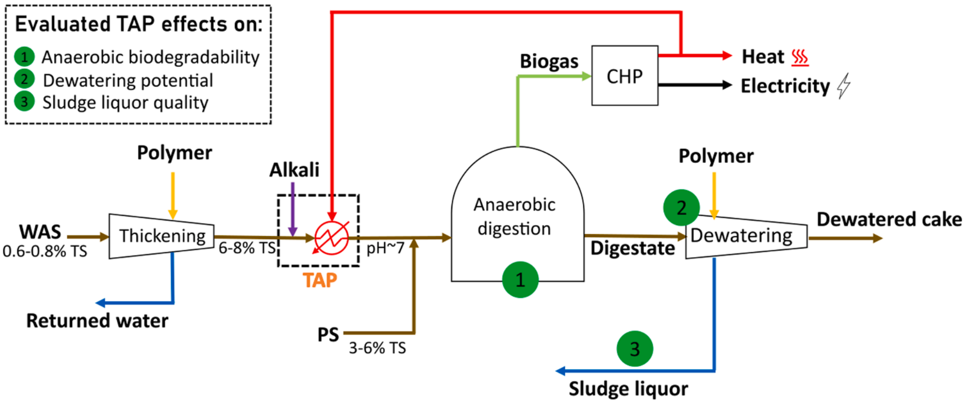

Fig. 1. Process flow diagram of sludge treatment line including thermal alkaline pretreatment (TAP) before anaerobic digestion.

Table 3
Process conditions of thermal alkaline pretreatment process of Pondus® (Pondus Verfahrenstechnik GmbH, Germany).

Parameter	Unit	Value
Temperature	°C	65–70
Alkali type	–	NaOH (50% w/w)
Alkali dosage	mg NaOH[a] per g TS of WAS	12–32
Reaction time	h	2.0–2.5
TS of input WAS	%	6–8
pH of WAS after TAP	–	6.8–7.0

[a] 100% purity.

that researchers use recognized standard methods for batch and continuous AD tests to make it easier for authentic cross-checking of results from different studies. Holliger et al. (2016) has proposed a procedure for a standardized biomethane potential test. It contains necessary information regarding different steps of batch biogas measurement from substrate preparation to analysis,validation and reporting of data (Holliger et al., 2021). Moreover, guideline of association of German engineers for fermentation of organic material is another source which describes all steps of a standard biogas measurement system for batch and continuous digestion processes (VDI, 2016).

2.1.1. Effect of initial biodegradability of WAS

One of the main incentives of TAP is enhancing BY which directly relates to reduction in organic solids. Regarding relative (%) BY increase after TAP of WAS, there is a wide range of results in literature. Effect of different ranges of initial biodegradability on relative BY increase is shown in Fig. 2. Non-parametric statistical test of Kruskal-Wallis (Table S2) showed a significant difference between average relative BY increase of different initial biodegradability ranges ($p < 0.05$). Dunn's post-hoc comparison test (Table S3) between different groups showed that range of 0–50 L CH_4 per kg added volatile solids (VS_{added}) is significantly different ($p < 0.05$) from ranges of 50–100, 200–250 and 250–300 L CH_4 per kg VS_{added}. Moreover, range of 100–150 L CH_4 per kg VS_{added} has a significantly different average from range of 200–250 L CH_4 per kg VS_{added}. All other inter-group differences were insignificant ($p > 0.05$). The significant difference between average relative BY increase related to lower and upper end ranges of initial biodegradability implies that there is a decreasing trend in between. This has also been previously reported in thermal hydrolysis by Carrere et al. (2008). In their study, they observed a significant decreasing trend in BY with increase in initial biodegradability of WAS from six WWTPs. Initial anaerobic biodegradability of WAS is per se dependent on various parameters including raw wastewater characteristics, types and configurations of treatment processes, and operational conditions of WWTP (e.g., sludge age). Another point of Fig. 2 is that upper ends of box plots are more dependent on initial biodegradability than lower ends.

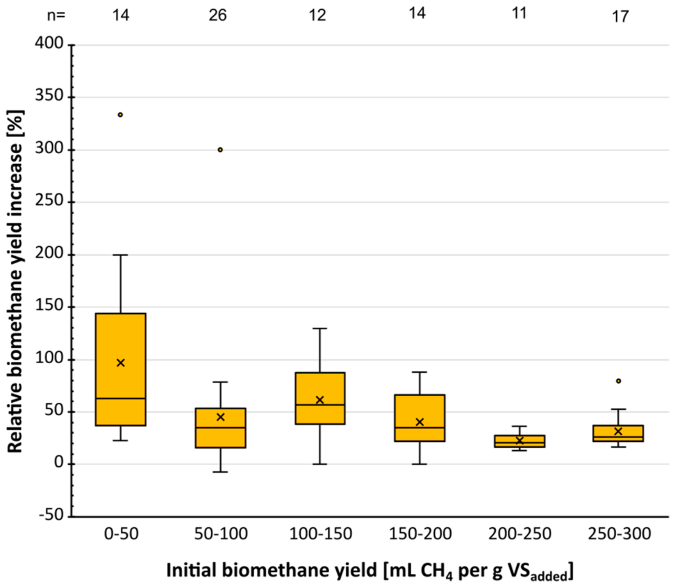

Fig. 2. Effect of different ranges of initial biomethane yield on relative biomethane yield increase after thermal alkaline pretreatment (Lines in box plots represent minimum, 25%, 50% and 75% quartiles and maximum. *x* and ° represent average and outliers, respectively. *n* is number of data points. List of data references in Table S1 of supplementary material).

Overall, average relative BY increase was between 22–97% depending on initial biodegradability of sludge (Fig. 2). Researchers sometimes reference their individual results to relative BY increases in literature for comparison or validation purposes, but this direct comparison needs more careful considerations. Therefore, it is strongly recommended, that researchers also compare initial biodegradability of sludge, when comparing results of their relative BY increase after TAP to those of other studies with different source of sludge. It should be noted that data in Fig. 2 are from TAPs of all ranges of temperature, alkali dosage and treatment time.

2.1.2. Effect of treatment temperature

As mentioned earlier, to examine effect of temperature ranges on BY, absolute BY increase after TAP was chosen as target parameter. Effect of temperature on absolute BY increase of TAP studies has been shown in Fig. 3a. Kruskal–Wallis test (Table S4) showed that there was no significant difference between means of different temperature ranges ($p > 0.05$). Accordingly, in terms of absolute BY increase, temperatures below 100 °C showed to have comparable results to temperatures above 100 °C. This means synergies between chemical and thermal effects

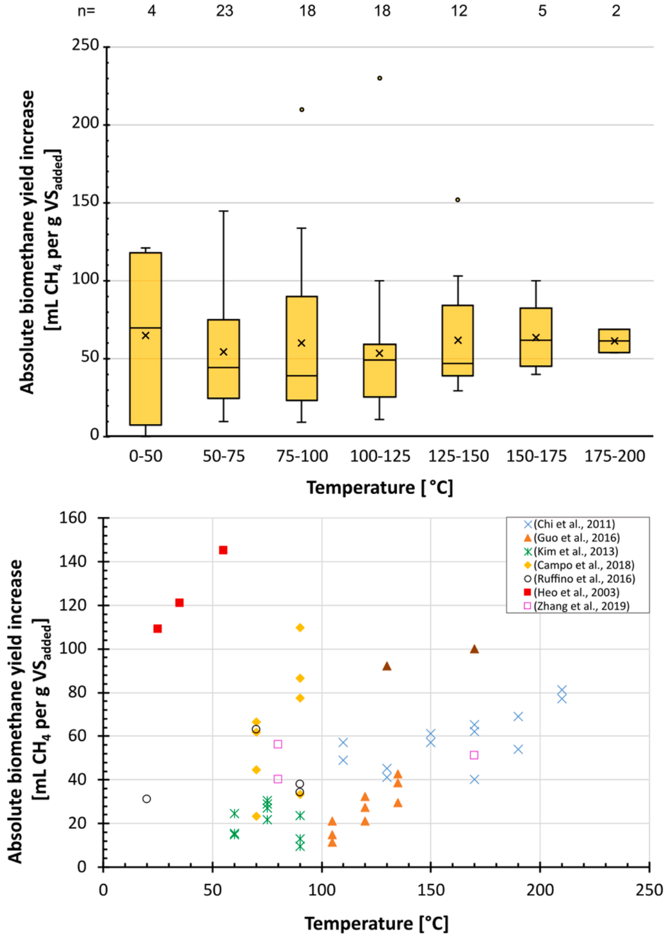

Fig. 3. a) Effect of different temperature ranges in thermal alkaline pretreatment on absolute biomethane yield increase (Lines in box plots represent minimum, 25%, 50% and 75% quartiles and maximum. *x* and ° represent average and outliers, respectively. *n* is number of data points. List of data references in Table S1 of supplementary material) b) Effect of increase of temperature on absolute biomethane yield increase from individual studies (data from Chi et al., 2011; Guo et al., 2016; Kim et al., 2013; Campo et al., 2018; Ruffino et al., 2016; Heo et al., 2003; Zhang et al., 2019; Valo et al., 2004).

seemed to show no further improvement for temperatures above 100 °C. This is not the same as with TH process, which has been shown to have an optimum temperature range around 160–180 °C regarding BY increase (Bougrier et al., 2008). Above these temperatures, formation of refractory organic matter enhances, which leads to decreased anaerobic biodegradability of sludge (Carrere et al., 2010). Adding alkali to the process, increases the possibility of these unwanted organic matter (Delgenès et al., 2000; Penaud et al., 1999; Penaud et al., 2000). Below these temperatures, BY decreases due to reduced sludge disintegration and solubilization effect (Devos et al., 2020).

To take a closer look at the effect of temperature in TAP, individual BY increase (measurement points) of multiple studies are separately shown in Fig. 3b. As it can be seen, BY enhances as temperature increases in each study. However, all these studies investigated temperature ranges either >100 °C or <100 °C, except for one study by Zhang et al. (2019). They compared low temperature thermal pretreatment (80 °C, 12 h) with low temperature TAP (80 °C, 154 mg NaOH per g TS, 1.3 h) and high temperature TH (170, 30 min). BY increase of 16.1%, 22.8% and 20.4% was reported for these three pretreatments, respectively. This study showed that low temperature TAP can yield even more biogas than energy intensive high temperature TH. Toutian et al. (2018) has also shown that low temperature TAP (80 mg NaOH per g TS, 70 °C, 2 h) and high temperature TH (170 °C, 30 min) show comparable BY increases in batch tests (+25% und +26%, respectively). This is an advantage for low temperature TAP in comparison to high temperature TH in terms of energy consumption (DWA, 2016). Moreover, safety issues regarding high temperatures and pressures are omitted, which promotes its popularity for full scale installations on WWTPs. However, it should be noted that low temperature TAP is associated with hazardous chemical handling (transport, storage, dosing, etc.), while in TH no chemicals are used. Nevertheless, more systematic research investigating BY increase after low temperature TAP and high temperature TH with same sludge still enriches available data in literature.

2.1.3. Effect of alkali type and dosage

Regarding alkali type, there was no research study, which compared the effect of different alkali types on BY, directly. This might be due to the fact that, $Ca(OH)_2$ and $Mg(OH)_2$ have shown to be less efficient than KOH and NaOH in solubilization degrees after TAP (Campo et al., 2018; Huang et al., 2016; Li et al., 2008; Mancuso et al., 2019; Penaud et al., 1999; Ruffino et al., 2016; Wang et al., 2016a). Moreover, alkalis with divalent cations such as $Ca(OH)_2$ and $Mg(OH)_2$ are preferably avoided due to promoting precipitation of struvite, brucite, etc. in digesters and downstream pipeline and equipment (Heinzmann and Engel, 2006). Finally, Between KOH and NaOH, the latter is preferred due to lower chemical costs and lower resource value of sodium in comparison to potassium.

Apart from alkali type, alkali dosage also plays a significant role on the economics of a TAP process as an operational cost factor. While some researchers have chosen to dose alkali based on pH as target parameter to study the effect of different pHs on BY (Dong et al., 2016; Kavitha et al., 2017; Li et al., 2017a; Liu et al., 2019; Nagle et al., 1992; Wang et al., 2018; Xiao et al., 2017), some others have investigated the effect of alkali dosage based on TS of sludge (Campo et al., 2018; Demir, 2018; Guo et al., 2016; Nagler et al., 2016; Ruffino et al., 2016; Zawieja, 2019; Zhang et al., 2015). This makes comparison of these studies difficult, as pH of sludge reduces with proceeding of TAP due to release of organic acids from sludge. Organic acids are produced from VS which is itself part of TS. Therefore, it is recommended that researchers use alkali dosage based on VS of sludge as a more fixed and unified parameter, beside pH. This makes it easier for comparison of alkali consumption among different studies, too. However, TS has been used throughout this study due to being more usual parameter used in literature.

To understand the effect of alkali dosage on BY, it is firstly needed to clarify the relationship between pH and alkali dosage. As per theoretical relationship between pH and alkali dosage for pure water (assumed that water has 7%TS with zero buffer capacity and no release of organic acids from its solid content), nearly 6–60 mg NaOH per g TS is needed to increase pH of water to 12–13 (for an effective disintegration as discussed later). To see how these ranges compare to ranges for real WAS, experimental relationship between alkali dosage and pH of real sludge with two different TS percentages is shown in Fig. 4 (not published data by authors; measurement method description in supplementary material, but briefly: pH measured after adding alkali to WAS and mixing). For WAS with 1.7% and 7.7% TS, the alkali dosage to increase pH of sludge to 12 was at least 50 and 70 mg NaOH per g TS, respectively, which is higher than the mentioned ranges for pure water. This is to be expected, since buffer capacity of WAS (e.g. bicarbonate) and abrupt release of organic acids consume part of dosed alkali. Pondus with 12–32 mg NaOH per g TS suggests a less alkali dosage range for a well-designed TAP (Table 3 and Fig. 4) in order to benefit from self-neutralization effect. With initiation of TAP, alkali addition increases pH of WAS. Following, release of organic acids due to disintegration of microbial cells neutralizes WAS (self-neutralization effect) during TAP. This is especially essential as sludge needs to be within neutral pH zone before sending to AD process. When alkali dosage surpasses a certain point an extra neutralization step with acids is needed after completion of TAP and before AD. This worsens economics of TAP (mechanisms are discussed in detail in Section 4). Majority of TAP studies needed to

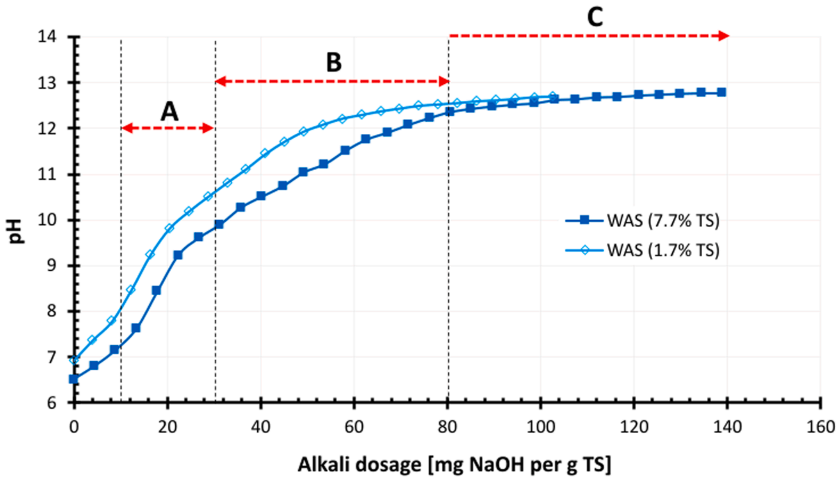

Fig. 4. Experimental relationship between alkali dosage and pH of real WAS with two different TS percentages (pH measured after dosing NaOH and mixing). A) Suggested alkali dosage range by Pondus leading to self-neutralization and TAP effluent pH of 6.8–7.0 B) Alkali dosage range with further meaningful increase in pH of WAS after dosing. However, with increase of alkali dosage in this range, self-neutralization does not suffice which leads to increase in pH of TAP effluent C) alkali dosage range with no meaningful increase in pH of WAS after dosing and not economical.

neutralize pretreated sludge with extra acids before AD (Chen et al., 2020; Kim et al., 2003; Kim et al., 2013; Liu et al., 2019; Park et al., 2005; Wang et al., 2018). Only a few studies did not need to neutralize sludge after pretreatment with acids (self-neutralization sufficed). These studies specifically used low levels of alkali dosage (<40 mg NaOH per g TS). These included Toutian et al. (2020a) and Li et al. (2017b) who practiced Pondus® in pilot and full-scale, respectively (12–32 mg NaOH per g TS). Moreover, Nagler et al. (2016) and Campo et al. (2018) reported on direct AD of pretreated WAS after TAP without neutralization with 32 and 40 mg NaOH per g TS. Beyond the alkali dosage range proposed by Pondus®, i.e. 32 up to 80 mg NaOH per g TS, pH of WAS still increases meaningfully (Fig. 4). However, effect of self-neutralization starts to decrease with increase of alkali dosage in this range. This is due to limited amount of releasable organic acids in WAS (more details in Section 4.2). Therefore, as shown in Fig. 4, for alkali dosage between 0 and 80, it should be tested to see which dosage leads to self-neutralization of pretreated WAS in TAP effluent, whilst achieving high enough pH right after dosing alkali. Dosing alkali beyond 80 mg NaOH per g TS has no significant effect on final pH and should be avoided to limit chemical costs.

Effect of different alkali dosage ranges in TAP on absolute BY increase is shown in Fig. 5a. Kruskal–Wallis test (Table S6) showed a statistically significant difference between alkali dosage ranges ($p < 0.001$). Dunn's post-hoc comparison test (Table S7) between different groups showed that only alkali dosage of 40–60 mg NaOH per g TS is significantly different ($p < 0.05$) from dosages of 0–20, 20–40 and 400–700 mg NaOH per g TS. All other inter-group differences were insignificant ($p > 0.05$). As shown in Fig. 5a, as alkali dosage increases from 0–20 up to 20–40 and 40–60 mg NaOH per g TS, BY also increases to its maximum values. This increase is due to solubilization enhancement of carbohydrates and proteins as alkali dosage increases (Kim et al., 2003; Li et al., 2008; Rani et al., 2012; Shehu et al., 2012). Afterwards, with further increase in alkali dosage, BY is negatively affected and starts to decrease. It should be noted that error bars of ranges of 40–60 (for upper and lower end), 60–100 (for upper end) and 100–200 mg NaOH per g TS (for lower end) are wider than others. This indicates the variability of data for these ranges which might attribute to impact of other parameters (e.g. temperature, which is not considered in Fig. 5a and b). Thus, above-mentioned interpretations should be considered with caution. Decrease in BY in higher alkali dosages is due to formation of refractory organic matter known as melanoidins (recognizable from produced brown color and aroma), which are the products of Maillard reactions (Echavarría et al., 2012). These complex set of reactions, long known and researched for their application in food industry are initiated by reaction of carbonyl and amine compounds (e.g. sugars and amino acids) after heating (Chung et al., 1986). According to Fig. 4, rate of pH increase falls beyond alkali dosage of 80 mg NaOH per g TS. Therefore, decrease in anaerobic biodegradability and formation of melanoidins is not dependent of pH in high alkali dosages. It might be possible, that reactions and mechanisms leading to formation of these matter vary with alkali dosage increase. This interpretation needs more fundamental

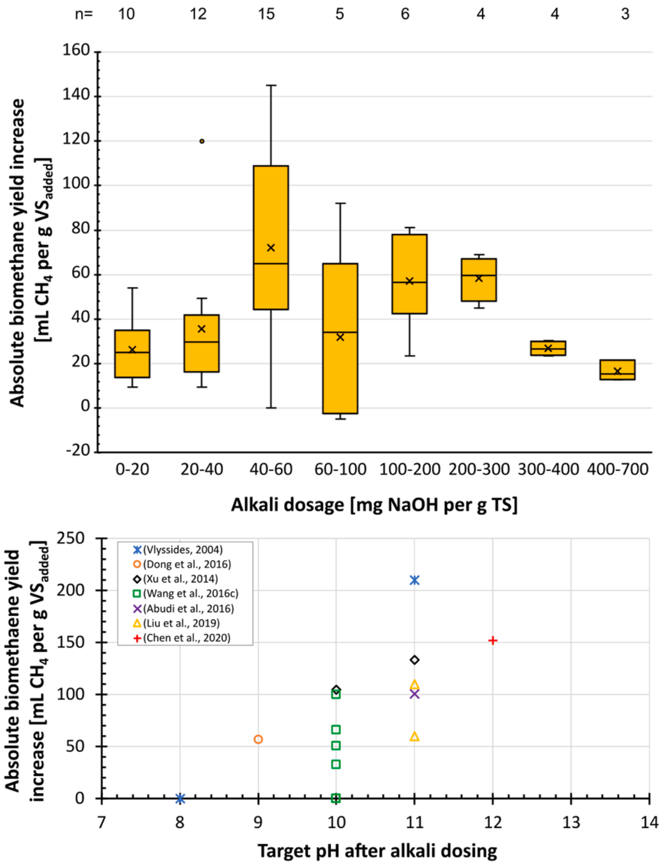

Fig. 5. a) Effect of different alkali dosage ranges in thermal alkaline pretreatment on absolute biomethane increase. (Lines in box plots represent minimum, 25%, 50% and 75% quartiles and maximum. *x* and ° represent average and outliers, respectively. *n* is number of data points. List of data references in Table S1 of supplementary material) b) Effect of pH in thermal alkaline pretreatment on absolute biomethane increase (data from Vlyssides, 2004; Dong et al., 2016; Xu et al., 2014; Wang et al., 2016c; Abudi et al., 2016; Liu et al., 2019; Chen et al., 2020).

research to clarify background mechanisms. Nevertheless, high alkali dosage leads to promotion of melanoidins formation (Ajandouz et al., 2001; Ajandouz et al., 2008), thus reducing anaerobic biodegradability (Delgenès et al., 2000; Penaud et al., 1999; Penaud et al., 2000). Therefore, it is recommended to keep the alkali dosage below 80 mg NaOH per g TS to avoid decreasing anaerobic biodegradability of WAS and possible increase of recalcitrant matter, beside economic savings.

Effect of pH on absolute BY increase is shown in Fig. 5b. pH has a significant increasing effect ($p = 0.005$) on BY (Table S8). This clearly shows that it is required to increase the pH of sludge to high levels (11 and 12) in the beginning of TAP to maximize the effect on solubilization of organic matter leading to biodegradability enhancement in AD. This corresponds to alkali dosage range of 50–70 mg NaOH per g TS (for WAS with 7.7%TS) according to Fig. 4. It should be noted that as the effect of high pH on disintegration of sludge is abrupt (Navia et al., 2002), it is not needed to keep this pH up for a certain time by constant dosing. Since this has no meaningful effect on disintegration efficiency and leads to worsening economics of TAP (through both extra alkali and acid consumption for neutralization), if not failure of AD (Wang et al., 2018).

For mechanisms of hydrolysis reactions there are two speculations. First, by adding alkali agent (such as NaOH) to WAS, and increasing pH high enough (>12), concertation of hydroxide ion OH^- goes extremely high. The abrupt strong concentration difference of OH^- around the semi-permeable cell membrane causes an osmotic shock. Subsequently, water molecules exit the cell through membrane to compensate for concentration difference leading to decrease of turgor pressure and eventual destruction of cell membrane. Finally, intracellular organic macromolecules release into liquid phase. Second, cell membranes in WAS microorganisms are composed of phospholipid bilayers, proteins, and carbohydrates. Lipid (or fats), which are esters of glycerol, and three long chain carboxylic acids (fatty acids) are attacked by hydroxide ions. This process (Saponification) is a chain of reactions in which fats are converted to alcohol and soap when exposed to a strong alkali agent such as NaOH and heat. Therefore, it is indeed pH which should be maximized (without introducing too much alkali) to maximize the disintegration effect. Alkali dosage is used as a parameter to indicate alkali consumption to reach this pH and not overdosing sludge (self-neutralization failure).

In conclusion, targeted pH and alkali dosage both have an important effect on anaerobic biodegradability of WAS. With an optimized alkali dosage (below 80 mg NaOH per g TS) for a maximum targeted pH through proper design of TAP (details in Section 4), alkali consumption is reduced significantly, while removing further step of neutralization of sludge with acids. Moreover, anaerobic biodegradability is maximized, and formation of recalcitrant organic matter is reduced. Process conditions of Pondus® has shown to be well designed to achieve this goal (Table 3 and Fig. 1).

2.1.4. *Effect of treatment time*

Treatment time (or reaction time) is one of the main factors in capital costs of a pretreatment process which determines required reactor volume. Although for some treatment techniques such as microwave or ultrasound, it also has a direct effect on energy consumption as an operating cost factor. For thermal and chemical pretreatments, its main effect is on reactor volume, when the reactor is thermally insulated. It is extensively reported that for high temperature pretreatments such as TH, treatment times around 30 min are enough for increase of anaerobic biodegradability (Donoso-Bravo et al., 2011; Li and Noike, 1992; Perez-Elvira et al., 2015; Sapkaite et al., 2017). Increasing treatment time beyond this threshold enhances solubilization of organic matter but has no significant effect on BY increase. Moreover, it also leads to increase of solubilized recalcitrant organic matter. However, as temperature decreases (specifically for $T < 100$ °C), the efficiency of pretreatment declines, thus demanding longer treatment times for compensation (Pilli et al., 2014). Therefore, for low temperature thermal pretreatments, treatment times up to several hours have also been investigated. Ferrer et al. (2009) showed that 9 h thermal pretreatment of raw sludge at 70 °C leads to 30% increase in BY in thermophilic AD which was more than BY values of 24 h, 48 h and 72 h pretreatment times. This indicates that there is a limit in pretreatment time for low temperature thermal pretreatment. On the other hand, as alkali compensates for low temperatures in TAP in relation to solubilization efficiency, treatment time could be lessened more with NaOH dosing. Zhang et al. (2019) showed that TAP (80 °C, with NaOH) for 1.3 h increased relative BY up to 56%, while only thermal pretreatment (80 °C) for 12 h led to 40% increase in relative BY. Hence, treatment time could be reduced by a factor of 10 after adding NaOH to reach comparable BY increase effect.

Fig. 6 shows the effect of treatment time on absolute BY increase. Kruskal–Wallis test (Table S9) showed there was no significant difference between means of different treatment times ($p > 0.05$). However, while treatment time equal or less than 0.5 h has been dominantly practiced for high temperature TAPs, treatment time range of 1.5–5.0 h is the optimal range for low temperature TAPs, in terms of maximum BY and reaching self-neutralization point of pretreated sludge before AD. After fixing temperature and alkali dosage, treatment time could be varied in this range to determine self-neutralization point of sludge. Pondus® as a low temperature TAP (70 °C) demands treatment time of 2.0–2.5 h, which falls within this range. In similar TAP studies (70 °C), which did not demand neutralization of WAS after TAP, treatment time was 1 h (Nagler et al., 2016) and 1.5 h (Campo et al., 2018). Nevertheless, even at low temperatures, treatment time should be as low as possible while maximizing BY to reduce formation of recalcitrant organic matter.

To conclude Section 2.1, optimum conditions of TAP for maximum BY increase of WAS have shown to be temperatures below 100°, alkali dosages below 80 mg NaOH per g TS and treatment time of 1.5–5.0 h. Furthermore, the goal should be achieving neutralization of sludge after TAP (without using acids) to improve economics of process. These limited ranges also help reduce formation of refractory organic matter. Best combination of conditions within these ranges should be further determined experimentally through optimization methods for each sludge sample.

2.2. *Composition of biogas*

Theoretical biogas composition is dependent on the stoichiometry of

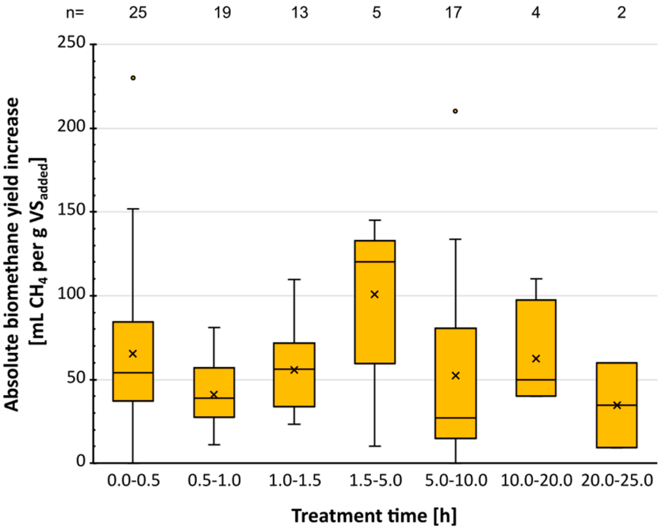

Fig. 6. Effect of treatment time ranges in thermal alkaline pretreatment on absolute biomethane increase. (Lines in box plots represent minimum, 25%, 50% and 75% quartiles and maximum. *x* and ° represent average and outliers, respectively. *n* is number of data points. List of data references in Table S1 of supplementary material).

biogas production reaction taking place in AD and elemental composition of substrate, according to Buswell equation (Chernicharo, 2007). Elemental composition of sludge does not change drastically after pretreatments. Therefore, biogas composition is not significantly affected by pretreatment processes including TAP, which is also reflected in literature (Guo et al., 2017; Kim et al., 2003; Park et al., 2014; Shehu et al., 2012; Toutian et al., 2020a). Nonetheless, due to some changes in alkalinity and equilibrium of buffering reactions in AD, some slight alterations in CH_4/CO_2 percentage or concentration of trace gases (NH_3, H_2S, etc.) could take place (Campo et al., 2018; Chen et al., 2020).

2.3. *Kinetics of biomethane production*

The main purpose of AD is in fact maximum stabilization of sludge, meaning minimizing degradation potential of its organic content before disposal (DWA, 2014). Single stage AD is known to be a complex process of four hydrolytical and biochemical stages occurring concomitantly, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis (Rosenwinkel et al., 2015). Pretreatment processes have proven to accelerate the hydrolysis step, which is indeed the rate-limiting stage for process design and retention times (Gonzalez et al., 2018). Nevertheless, it should be separately considered, to what extent a pretreatment process affects kinetics of the whole AD process and not only the hydrolysis step.

Overall kinetics of full AD after implementing TAP is improved, if two conditions are fulfilled. First, same stabilization degree of sludge as that of without TAP in shorter time is achieved. Second, sludge liquor contains same soluble chemical oxygen demand (COD) as that of without TAP. In this case, digester volume reduces and overall retention time decreases. For more clarification, Fig. 7 schematically shows different BY curves for WAS with and without pretreatment for a normal AD. Most studies of TAP show BY curves similar to curve number 3 after pretreatments, leading to an increase of final BY (Chi et al., 2011; Liu et al., 2019; Liu et al., 2020; Nagler et al., 2016). However, curve number 3 does not lead to reduction of time required for same stabilization degree of sludge as that of without TAP, since it needs as much time as needed by not pretreated WAS (curve number 1). This might be due to inherent process limitations of AD. Maximum biogas yield in complex biological system of AD is a result of healthy syntrophy of all participating microorganisms and ongoing biochemical processes. This necessitates that all affecting parameters (pH, VFAs, alkalinity, ammonia, microbial populations, etc.) are in certain ranges. Any deviation from these suitable ranges results in a slight inhibition in biomethane production (Appels et al., 2008; Chen et al., 2008). Therefore, significant increase of solubilized organic matter accessible to microorganisms after pretreatment does not necessarily mean that they convert it all faster to biogas.

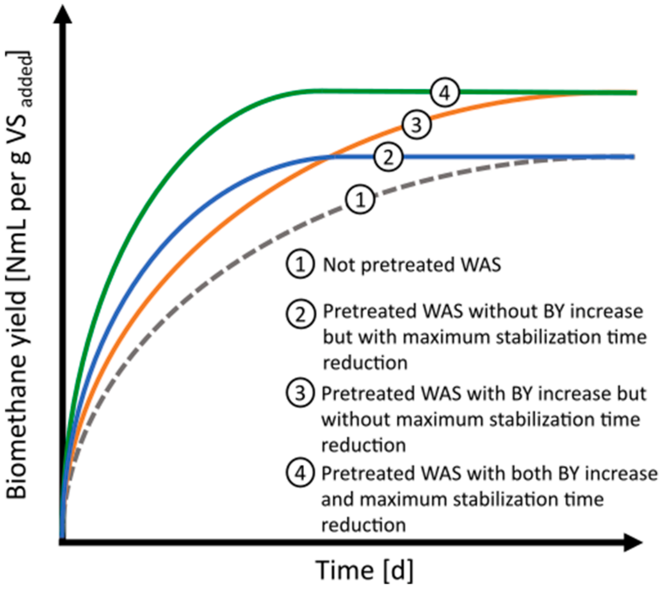

Fig. 7. Schematic illustration of kinetics of biomethane production of WAS with and without pretreatment and its effect on maximum stabilization time reduction.

In contrast to curve number 3 and ideally preferred, curve number 4 represents a pretreatment which leads to increased BY and enhanced kinetics of AD, with reduction of digestion volume (due to less time needed for maximum stabilization). Curve number 2 represents increase of kinetics of AD and reduction of digestion volume (with maximum stabilization degree), but without increase in BY. Biomethane potential curves similar to curves number 2 and 4 were not found in literature after TAP. This implies that increase in kinetics of hydrolysis step (enhanced solubilization) after TAP, does not necessarily lead to reduction of time (or digestion volume). This is also recognizable from multiple peaks in curves of daily biomethane production rates of batch biomethane potential tests (Guo et al., 2016; Guo et al., 2017; Zhang et al., 2015). These peaks represent temporary inhibition of methanogenesis which could be due to concentration increase of metabolite precursors of methanogenesis step (i.e. volatile fatty acids, acetate, H_2). The reason for this hypothesis is that as the inhibition factor is relieved (i.e. consumption of these precursors), biomethane production rate increases again. However, conclusive statements regarding authentic causing reasons need further systematic research.

Liu et al. (2020) calculated kinetic rates of four main stages of semi-continuous AD after TAP for three hydraulic retention times (HRT) of 25, 20 and 15 days, recently. It was shown that decreasing HRT led to significant increase of soluble COD in hydrolysis step of AD (44.1–155.6% for TAP pretreated sludge relative to not pretreated sludge), while slightly decreased the kinetics of other three steps of acidogenesis, acetogenesis and methanogenesis (0.1–13.9%). This indicated that after pretreatments, reduction of HRT of AD could lead to increase of soluble COD in sludge liquor. This was accompanied by reduction of methane production kinetics to a slighter degree, although final BY was still higher than that of sludge without pretreatment. In this regard, more systematic research still enlightens the effects of TAP on reduction of HRT needed for AD with maximum stabilization.

2.4. *Other issues*

Digester volume is mainly dependent on sludge retention time (i.e. HRT) and volumetric flow of feed. Volumetric flow of feed is itself dependent on its water content (or TS). AD is normally fed with maximum 4–7% TS after mixing mechanically thickened WAS and primary sludge (PS) (ATV, 1996). This limit is due to high viscosity of sludge in higher TS contents which hinders mass and heat transport in digester lowering its efficiency. Viscosity of sludge has shown to decrease significantly during low temperature TAP (Tan and Li, 2017; Wang et al., 2016b). This fact can be used to double the digestion capacity. To actualize this, WAS should be highly dewatered (>15% TS) before TAP. This would be similar to TH, in which AD of sludge with 10% TS is possible due to significant viscosity reduction (Barber, 2016), above which AD is prone to inhibition risks. Therefore, low temperature TAP of highly dewatered WAS with subsequent high solids AD (~10% TS) should be investigated, as a promising alternative to TH in terms of doubling digestion capacity.

One of the challenging issues regarding operation of AD and activated sludge systems is combating foam production (Ganidi et al., 2009; Subramanian and Pagilla, 2015), especially during winter months. Different operational issues in activated sludge systems lead to enrichment of filamentous bacteria which are responsible for promotion of foam production. After being transported from activated sludge tanks to digestion tanks as WAS, they become more problematic. Foaming problem significantly hinders biogas production and increases the operating costs (e.g. through antifoam addition). According to plant operators in Germany (personal communications) TAP (Pondus®) has shown to be effective in suppression of foam production. However, due to lack of information in literature, systematic research is needed to address its efficiency and mechanisms on foam reduction in AD or activated sludge tanks.

For countries, where digested sludge utilization in agriculture is legally allowed, effect of TAP on odor suppression and hygienization of digestate is also an area, which lacks information in literature and needs more research.

Table 4

Summary of literature dewaterability results after thermal alkaline or alkaline pretreatment of sludge before or after anaerobic digestion.

Before/After anaerobic digestion (BAD/AAD)	Scale	Sludge type (TS %)	Temperature (°C)	Time (h)	Alkali reagent	Alkali dosage (mg per g TS)	pH	Dewaterability results	Reference
AAD[b]	Full-scale	WAS (6–7%)	65–70	2–2.5	NaOH	12–32	–	Improvement by 2.5% points with maximum cake solids of 31%. Cake solids increased from 24.7 to 28.6% TS as polymer dosage increased from 10.9 to 17.5 kg per t TS.	(Li et al., 2017b)
AAD[b]	Pilot	WAS (6.5%)	65–70	2–2.5	NaOH	12–32	–	No increase in TS of sludge cake after centrifugation with same polymer dosage.	(Toutian et al., 2020a)
AAD[b]	Lab	WAS (4–6%)	70	1	NaOH	32	–	Dewaterability parameter DS(A) increased from 27.0 to 32.6% with polymer usage increase from 12.7 to 16 kg per t TS.	(Nagler et al., 2016)
AAD[b]	Lab	WAS (6–7%)	70	2	NaOH	12–32	–	Dewaterability parameter DS(A) increased from 26.7 to 31.3% with polymer usage increase from 11.2 to 13.3 kg per t TS.	(DWA, 2016)
AAD[b]	Lab	WAS (5.1%)	170	0.016	NaOH	50	–	Increase in flocculants need in dewatering test (centrifuge) from 13.1 kg per t TS for control to 23.4 kg per t TS for pretreated digested sludge.	(Chi et al., 2011)
AAD[a]	Lab	Mixed sludge (2%)	–	0.5, 1.0, 1.5, 2.0	NaOH	200	–	No change in TS of sludge cake (centrifuge with polymer) and turbidity of sludge liquors.	(Li et al., 2013)
AAD	Lab	WAS (2.8%)	–	–	NaOH and/or $Mg(OH)_2$	–	10	Deterioration of dewaterability in terms of CST with NaOH and significant improvement after adding $Mg(OH)_2$ (blank → 348 s, 100:0 (NaOH:$Mg(OH)_2$) → 546 s, 75:25 → 77 s).	(Huang et al., 2016)
AAD[a]	Lab	WAS + PS (2.1%)	35, 55	144	NaOH	–	8, 10, 12	At 35 °C, NCST of all digested sludges were almost the same and at 55 °C, NCST of untreated (no alkali) was higher than treated sludges at different pHs.	(Wang et al., 2018)
BAD and AAD[a]	Lab	WAS (1.1%)	–	0.5	NaOH	112, 200, 312, 488	10, 11, 12, 12.5	CST of disintegrated sludge increased with pH. CST decreased by 22% for digested sludge (microwave + pH 12)	(Dogan and Sanin, 2009)
BAD	Lab	Mixed sludge (6%)	20–120	1	NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$	36–68 (NaOH)	8–12	36 mg NaOH per g TS makes CST longer than blank. Best results were obtained for 100 °C, $Ca(OH)_2$ at pH = 10 and 60 min. CST decreased from 34 to 22 s with $Ca(OH)_2$. TS of sludge cake increased from 28% to 46%. Monovalent ions such as Na^+ and K^+ give longer CSTs.	(Neyens et al., 2003)
BAD	Lab	WAS	0–40	0–24	NaOH, $Ca(OH)_2$	0–1600 (NaOH), 0–2960 ($Ca(OH)_2$)	–	NaOH treatment: CST increases significantly for doses of 320 mg per g TS and then decreases to initial levels. Turbidity increases for dose of 160 mg per g TS and then decreases. Sludge cake solids changed very slightly (5–8%TS). $Ca(OH)_2$ treatment: CST and turbidity remain within initial levels. Sludge cake solids significantly improved from 8% to 35% TS)	(Li et al., 2008)
BAD	Lab and pilot	WAS 12.5%)	140–220	0.5–2.0	$Ca(OH)_2$	51–105	9–11	Dewaterability was improved with increasing pretreatment temperature but the impact of the pretreatment time was not significant (cake TS up to 26–42.5% for centrifuge and 39.5–69% for filter press, raw sludge 15%) for thermal pretreatments. Addition of $Ca(OH)_2$ gave better performance on the subsequent mechanical dewatering of the pretreated sludge compared to pure hydrothermal pretreatment, and the higher the pH value, the better the dewaterability of the pretreated sludge.	(Li et al., 2017a)
BAD	Lab	WAS (3%)	60, 80, 90	3, 6	NaOH	–	6–8, 10, 12	CST decreased from 2500 s to 1500 s after four successive steps of TAP and dewatering.	(Liu et al., 2017)

[a] With neutralization before AD.

[b] Without neutralization before AD.

3. Dewaterability and sludge liquor quality

3.1. Dewatering potential

Improving dewaterability of sludge was the main motivation of implementing early pretreatment techniques and still remains one of top costs saving incentives (Neyens and Baeyens, 2003). Dewaterability of digested sludge plays a significant role in reduction of costs related to final sludge disposal. Specifically, final wet mass of sludge and polymer consumption are impactful with 59% and 17% share on disposal costs (centrifuges) for WWTPs in Germany (DWA, 2011). Dewatering potential of sludge is evaluated by measuring TS of dewatered cake and TSS (total suspended solids) of liquor on WWTPs (DWA, 2008). It is desirable to maximize both of these parameters with optimal polymer use to yield a higher dewatered cake and less loaded liquor. Therefore, it is advised that researchers report on both dewatering potential parameters and polymer consumption, to make it easier for economic comparison of different studies. Mimicking real dewatering processes on WWTPs via lab-scale equipment is very challenging which makes dewatering potential difficult to be quantified. In this regard, Kopp and Dichtl (2001) developed a thermogravimetric method which predicts more precise results (parameter known as DS(A) ±1.5% deviation from real achievable TS). This method needs special equipment and procedure, calibration as well as personal experience. More simply measured parameters such as capillary suction time (CST), specific resistance to filtration (SRF) or TS of dewatered cake determined by lab centrifugation of a sludge sample have also been used by researchers. These parameters are usually used to compare effects of different process conditions on dewaterability potential. However, due to different conditions used by researchers, it is not easy to deduce conclusive remarks. Accordingly, it is highly recommended that experts develop and propose a unified standard method to measure sludge dewaterability in lab scale similar to that of biochemical methane potential by Holliger et al. (2016). Such a standard method can be used by researchers leading to more authentic comparisons between different studies.

Regarding effect of TAP on dewatering potential of digested sludge, there is not as much information in literature as for solubilization of organic matter or anaerobic biodegradability. A summary of results of dewatering performance after TAP or alkaline pretreatment is presented in Table 4. It should be noted that data regarding CST (or NCST) do not represent dewatering potential parameter on full scale WWTPs which is cake solids percentage. Therefore, they should be viewed only as results of sludge capability for water release. Results are categorized into two groups of dewaterability before AD (BAD) or after AD (AAD). Dewaterability after pretreatment and before AD is of interest for those WWTPs, where there is no AD in place and sludge is dewatered and disposed directly or sent to a central AD. In these scenarios dewatering liquor can be used as a carbon source for biological wastewater treatment process. According to BAD results, dewaterability generally tends to worsen if NaOH or KOH are used as alkali reagent. On the contrary, $Ca(OH)_2$ or $Mg(OH)_2$ improved dewaterability. This is probably due to decrease in ratio of monovalent to divalent cations, when $Ca(OH)_2$ or $Mg(OH)_2$ are used instead of NaOH or KOH which promotes final dewaterability (Higgins and Novak, 1997).

Dewaterability after AD is of more interest for WWTPs with AD in place. Results of dewatering potential after TAP showed to be ambiguous. Some TAP studies in full- and lab-scale showed improvements in dewaterability in terms of DS (A) parameter (DWA, 2016; Nagler et al., 2016). However, this was accompanied by increase in polymer usage due to increase of soluble matter. On the contrary, there were studies, in which no increase in dewaterability (Toutian et al., 2020a) or even deterioration (Huang et al., 2016) have been reported. It should be noted that measurement methods of these two studies were different, namely measurement of cake TS after lab centrifuge and measuring of CST, respectively. To come to more rigorous conclusions, further systematic research with standardized dewaterability test methods is needed. This is specifically a very important issue when comparing low temperature TAP to TH, since one of main and widely reported advantages of TH is improvement of dewaterability at high temperatures ($T > 160$ °C). To shed light into mechanisms through which low temperature TAP affects dewaterability, it would also be interesting to consider influencing parameters such as sludge age and mixing ratio (WAS:PS), sludge chemical characteristics (pH, buffering system and capacity, concentration of NH_4^+-N, $PO_4^{3-} - P$, Ca^{2+}, Mg^{2+}, CH_4, etc.), P-removal process type (biological or chemical), different EPS content and seasonal variations of sludge.

3.2. Sludge liquor quality

Complex organic matter is broken down by microorganisms to simpler products during AD. CH_4 and CO_2 are final products of carbonaceous organic matter degradation which are transported to gaseous phase as biogas. Organic nitrogen and phosphorous are degraded to ammonium and orthophosphate which remain solubilized in sludge liquor. TAP targets rigid cell membranes in WAS which leads to release of intracellular organic matter. This facilitates access of microorganisms to a higher fraction of organic matter. As a result, both organic and inorganic (particulate and soluble) loads of sludge liquor increase as reflected in increase of parameters total COD, soluble COD, total phosphorous, $PO_4^{3-} - P$, total nitrogen, $NH_4^+ - N$, and total suspended solids.

Part of load increase in sludge liquor is due to non-biodegradable organic matter such as refractory dissolved organic carbon, dissolved organic nitrogen or dissolved organic phosphorous. Since they cannot be removed by conventional process of wastewater treatment, they can pose a risk to concentration increase of the effluent quality parameters on WWTP (Dwyer et al., 2008). Knowing that discharge regulations are constantly subject to stricter limits, it is important to take this issue into account before implementing a pretreatment on WWTP. Toutian et al. (2020a) reported that Pondus® resulted in 0.8–1.1 mg/L increase in effluent sCOD of WWTPs in Berlin due to formation of refractory COD in TAP, while with TH (130–170 °C) this was 2–15 mg/L (Toutian et al., 2020b). This is expectable, considering lower temperature of Pondus® in comparison to TH which leads to less intensive Maillard reactions. There is not as much information for these parameters as for solubilization degrees and biomethane potentials in literature. Therefore, further research is needed to clarify to what extent different operating conditions of TAP affect WWTP effluent quality parameters. To do such measurements, pretreated WAS should be digested in continuous AD. Then, liquors from dewatering of digested sludge should be incubated in continuous aerobic tests which mimic conditions of activated sludge systems on a WWTP. This procedure should also be followed for a basis scenario in which not pretreated WAS is tested to make an authentic comparison on the effects of TAP. This leads to measurement of remaining not biodegradable nutrient fractions in wastewater which were introduced to system vie pretreatment process.

Regarding inorganic load increase in sludge liquor, mainly $NH_4^+ - N$ and $PO_4^{3-} - P$ concentrations should be considered, as these exert extra treatment costs (through aeration and chemicals) and additional required treatment capacity in the main-stream. Sludge liquor is usually directed to head of WWTP to be treated in main-stream. Alternatively, it can be first majorly treated in a separate stage through an added side-stream treatment process and then be directed to main-stream for further treatment. It should be noted that through innovative nutrient recovery processes, increase of $NH_4^+ - N$ and $PO_4^{3-} - P$ in sludge liquor can be utilized, positively. Especially for phosphorous as a critical nutrient, this benefits numerous commercialized processes which aim to recover phosphorous from digested sludge or its liquor. There is also a lack of sufficient information regarding increase of these nutrient in sludge liquor after TAP and further research is needed to show how TAP operating conditions increase sludge liquor quality parameters for more rigorous conclusions on its economic aspects. As an example, Toutian et al. (2020a) showed that after Pondus®, $NH_4^+ - N$ and $PO_4^{3-} - P$ increased 35% and 17%, respectively. These increases should be taken into consideration in economics studies.

4. Important process design parameters

Economic and efficient low temperature TAP process involves various factors which are closely related and should all be considered when investigating or designing this process (Fig. 8). Deviations from an optimal and correct design of TAP results in an inefficient process or worsen its economics. In following some of the important process design aspects of TAP are discussed in more details.

4.1. Total solids of WAS input to TAP

TS percentage of WAS plays a key role in economics and efficiency of TAP. Water as the necessary reaction medium in WAS facilitates mixing leading to better mass and heat transport. However, as TS of WAS increases, viscosity of WAS exponentially increases and sludge adopts more of a non-Newtonian fluid (Pseudo-plastic) behavior (Cao et al., 2016; Cheng and Li, 2015), which in turn worsens mixing and pumping efficiency. Luckily, after/during pretreatment viscosity of sludge already reduces due to disintegration of its microbial structure (Farno et al., 2016; Feng et al., 2017; Wang et al., 2016b).

On the contrary, water unfavorably consumes energy (e.g. heat) and reactive reagents (e.g. alkali) which are actually intended to affect the solids in WAS. The schematic relationship between TS percentage in sludge, its viscosity and heat/alkali consumption in TAP are shown in Fig. 9.

Regarding alkali consumption, pH plays the main role in terms of strength of reactive driving force as it directly reflects the concentration of OH^- in the liquid phase. Therefore, it is important to achieve a certain pH at start of pretreatment to apply the needed reactive ionic strength for attacking microbial biomass and to assure maximum disintegration potential of alkali. For a solid weight unit of WAS (e.g. 1 kg solids as a basis), required alkali reagent decreases, as its water content decreases (increase in TS). This is due to alkalinity capacity of sludge, which increases alkali consumption.

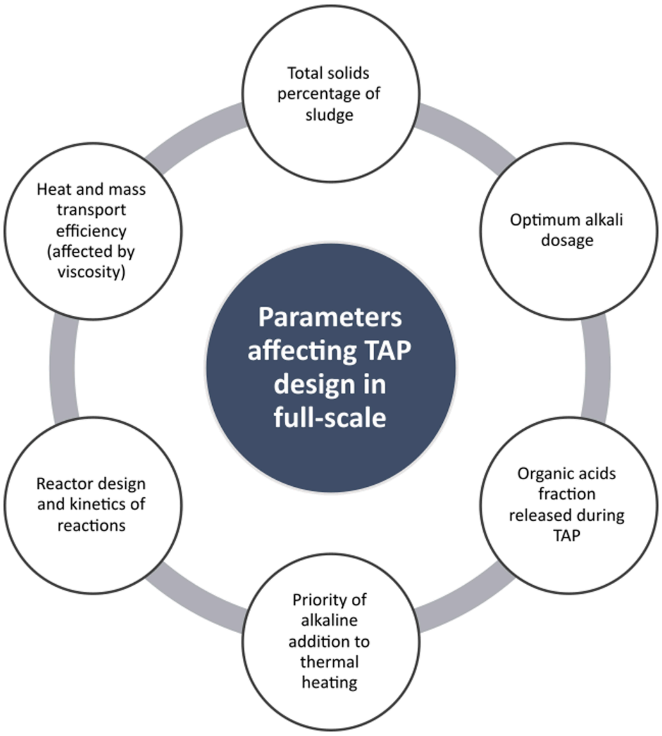

Fig. 8. Different linked parameters influencing thermal alkaline pretreatment design in full-scale.

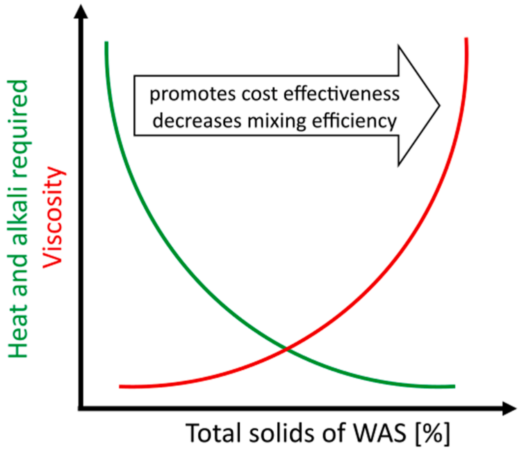

Fig. 9. Schematic relationship between viscosity and required heat and alkali reagent for thermal alkaline pretreatment vs. total solids percentage in sludge.

Alkali consumption is not the only parameter dependent on TS of WAS. Due to following neutral pH requirement (6.5–7.5) of sludge before AD, it is necessary to reduce pH of WAS after TAP. Although this can be done through adding inorganic acids (e.g. HCl), it is economically favorable to avoid this. Adding inorganic acids also increases inorganic solids due to formation of salts. The goal is to exploit potential of released organic acids during pretreatment to neutralize WAS after TAP (self-neutralization effect). Fraction of organic solids in sludge and subsequently its organic acid release yield during TAP is limited. Therefore, its solid content (or TS) should be high enough to allow for neutralization of pretreated thickened sludge and not to consume released organic acids for buffer capacity of extra liquor content in sludge.

Concerning heat consumption, amount of heat required to increase temperature of sludge up to a certain point in TAP directly correlates with volumetric flow rate of sludge. Barber (2016) showed crucial importance of reducing water content of sludge prior to TH on steam consumption reduction. That is in fact, the main reason of required pre-dewatering stage (up to 16–18% TS) prior to TH in full-scale.

As an example, Pondus® suggests increasing TS of WAS up to 6–8% before TAP. This eliminates excessive use of alkali, extra neutralization before AD and heating the digester through following procedure:

WAS has usually 0.6–0.8% TS after secondary clarifiers (DWA, 2014). In this range of TS, it contains a considerable amount of mechanically separable water which contributes to its significant large volumes. Therefore, it is normally thickened with dewatering equipment up to 6–8% TS. This reduces nearly 90% of its original volume contributing to significant subsequent digestion volume savings. Afterwards, WAS is pretreated through Pondus® process leading to hydrolyzed WAS with a final pH of 6.8–7.0 (due to its optimized operating conditions) and $T_{WAS} = 70$ °C. Following, pretreated WAS is mixed with same volume of PS (which normally has TS in range of 3–6% (DWA, 2014)) before sending to digester (leading to TS~5% and neutral pH). This leads to a sludge mixture with $T_2 = 40$ °C according to following equation:

$$\Delta\dot{Q} = \rho\dot{V}C(T_2 - T_{WAS}) + \rho\dot{V}C(T_2 - T_{PS}) = 0 \quad (1)$$

Assumptions here were: average temperature of PS being 10 °C (T_{PS}), density and heat capacity of WAS and PS being almost same due to >90% water content in both and fully insulated mixing chamber and digester. In this way, TAP+AD would need as much heating energy as an AD alone with optimized alkali dosage and no neutralization with acids.

Accordingly, there is an optimal range of TS percentage in WAS for TAP above which mass and energy transport efficiencies decline and below which energy and/or reactive reagents are excessively consumed. Therefore, researchers should take TS of sludge into account for a properly designed TAP and its techno-economic assessment.

4.2. *Optimum alkali dosage*

After thickening WAS to a certain TS, there is an optimum point (or range) for alkali reagent dosage to perform a complete and economic TAP. When dosed below this point, there would not be enough reactant (ionic strength) available to thoroughly disintegrate sludge (pH below maximum pH required for a full alkaline disintegration). Consequently, less disintegration products, i.e. organic acids, are released which in turn weakens self-neutralization process. By dosing alkali reagent above optimal point, disintegration process would be thorough. However, due to limited amount of released organic acids, sludge would not be able to self-neutralize that surplus amount of alkali. This in turn, necessitates extra step of neutralization with acids. On the contrary, in case of optimum dosage of alkali reagent, not only thermal alkaline disintegration is complete but also organic acids released are enough to self-neutralize sludge (Campo et al., 2018; Li et al., 2017b; Nagler et al., 2016; Toutian et al., 2020a). Hence, no additional costs of extra alkali or acid are necessary. This has also been graphically illustrated in Fig. 10 for further clarification. The progressions in Fig. 10 are only for illustration of optimum point of alkali dosage and real pathways (and above-mentioned mechanisms from authors) need to be verified by precise lab research. Pondus® consumes 12–32 mg NaOH per g TS of sludge, which is in the lowest range of alkali dosages reported for TAPs in literature.

4.3. *Alkali addition prior to thermal heating*

Regarding cost effectiveness of TAP, it is very important to carry out alkali dosing step before thermal heating. The reason lies again in release of organic acids from disintegration of microbial biomass into liquid phase leading to self-neutralization of sludge. When thermal heating is performed before adding alkali, a certain amount of organic acids are released which leads to reduction of pH. This in turn leads to two unfavorable issues. Firstly, there would be more alkali reagent needed for a complete alkaline disintegration (e.g. to increase pH up to 12), as some of alkali would be consumed for neutralization of released organic acids by foregoing thermal pretreatment. Secondly, since part of organic acids are already released by thermal pretreatment, there would not be sufficient acids released for self-neutralization of sludge after the following alkaline pretreatment. Consequently, extra acid addition would be needed to neutralize sludge before AD. This has been graphically illustrated in Fig. 11 for more clarification. Again, the progressions in Fig. 11 are only for illustration of this issue and real pathways (and above-mentioned mechanisms from authors) need to be determined by precise lab research. In Pondus®, alkali addition is performed before thermal heating as reported by (Heo et al., 2003; Li et al., 2017b; Nagler et al., 2016; Toutian et al., 2020a).

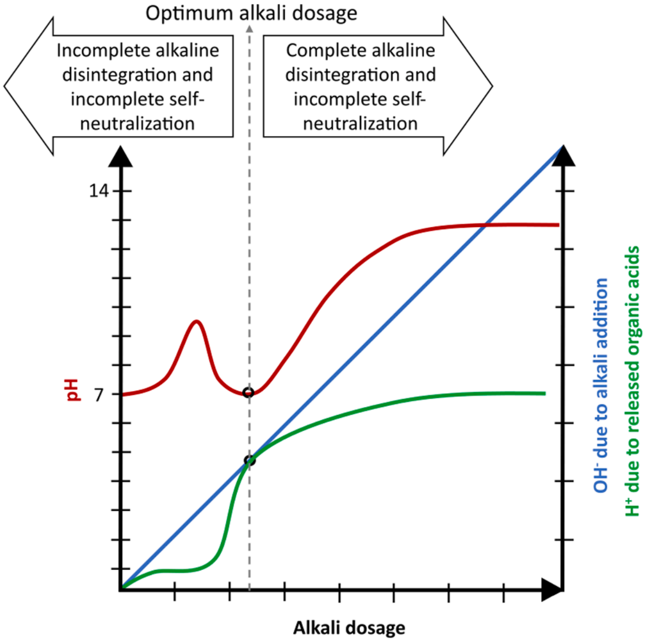

Fig. 10. Schematic probable illustration of pH of WAS and concentration of released OH^- and H^+ after thermal alkaline pretreatment versus alkali dosage.

5. Conclusions

Thermal alkaline pretreatment of WAS as a potential alternative to thermal hydrolysis was reviewed. Following conclusions were drawn:

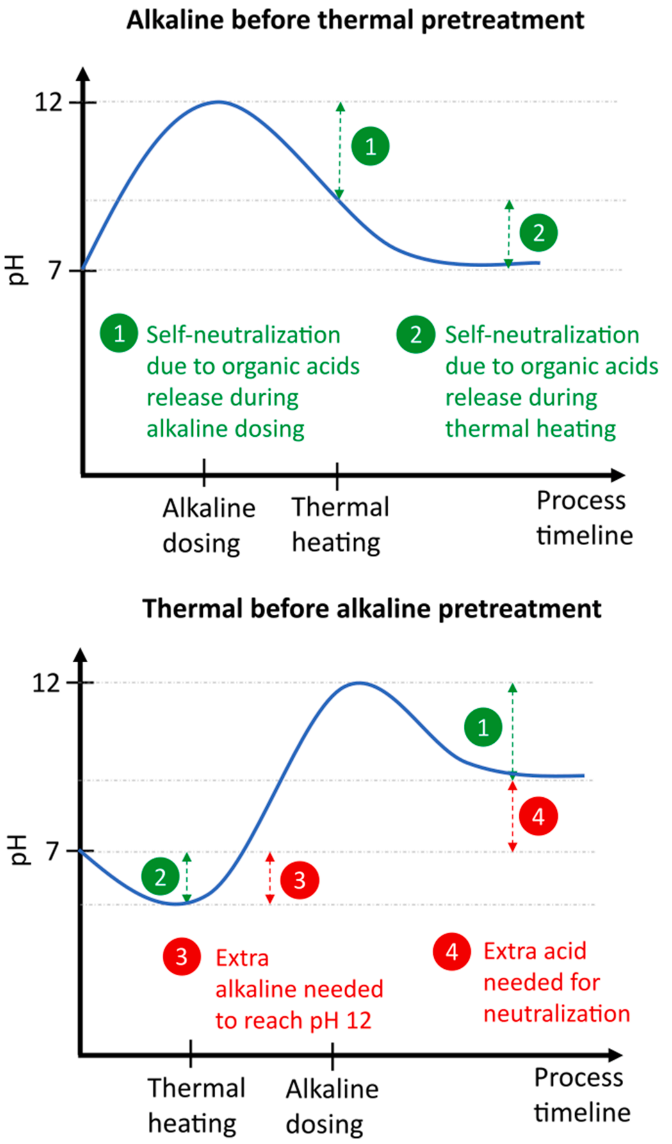

Fig. 11. Schematic probable illustration of importance of carrying out alkaline step before thermal heating step in thermal alkaline pretreatment to reduce extra alkali and acid costs.

- Biogas yield increase of WAS after pretreatment lessens as initial biodegradability of sludge increases. Depending on initial biodegradability, biogas yield increase of 22–97% is expected.
- Low temperature TAP ($T < 100$ °C) increases biogas yield to a comparable extent as of high temperature thermal hydrolysis ($T = 170$ °C).
- Alkali dosage and resulting initial pH have a significant effect on biogas yield. It is recommended to keep alkali dosage below 80 mg NaOH per g TS of WAS for maximum biomethane production and achieving self-neutralization after TAP. Keeping pH high by constant dosing of alkali should be avoided. It is advisable to dose alkali based on organic solid weight unit of sludge (e.g. mg NaOH per g VS sludge) instead of only adjusting to a fixed pH. This makes calculation of alkali consumption possible for comparison between studies.
- Treatment time between 1.5 and 5.0 h is sufficient for low temperature TAP. After fixing temperature and alkali dosage, treatment time can be varied in this range to achieve self-neutralization point after TAP.
- The potential benefit of TAP to reduce digestion time needed for maximum stabilization of WAS (kinetics evaluation of biogas production) cannot be confirmed and needs more research.
- Effect of low temperature TAP on dewatering potential of digestate seems to be ambiguous and needs more systematic research. Especially, final TS and polymer consumptions should be investigated for more rigorous conclusions. Therefore, a standardized method for dewaterability measurement in lab-scale should be developed for better comparability of results.
- Impact of TAP on sludge liquor quality parameters (dissolved nutrients as well as refractory organic matter), suppression of foaming in digester and hygienization of digestate needs more research.
- Optimized process conditions (temperature, alkali dosage and treatment time, TS of WAS and performing alkali dosing step before heating step) with goal of self-neutralization of WAS after TAP are key factors of an efficient and economic TAP.

Finally, despite extensive studies in literature and existing full-scale installations, TAP still needs more research for clarification of its underlying mechanisms, performance in terms of biogas yield increase and downstream effects on sludge dewaterability and liquor quality, and finally on its economic benefits for the WWTP operator.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2021.117465.

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