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Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives

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ABSTRACT

Sewage sludge management is now becoming a serious issue all over the world. Anaerobic digestion is a simple and well-studied process capable of biologically converting the chemical energy of sewage sludge into methane-rich biogas, as a carbon-neutral alternative to fossil fuels whilst destroying pathogens and removing odors. Hydrolysis is the rate-limiting step because of the sewage sludge complex floc structure (such as extracellular polymeric substances) and hard cell wall. To accelerate the rate-limiting hydrolysis and improve the efficiency of anaerobic digestion, various pretreatment technologies have been developed. This paper presents an up-to-date review of recent research achievements in the pretreatment technologies used for improving biogas production including mechanical (ultrasonic, microwave, electrokinetic and high-pressure homogenization), thermal, chemical (acidic, alkali, ozonation, Fenton and Fe(II)-activated persulfate oxidation), and biological options (temperature-phased anaerobic digestion and microbial electrolysis cell). The effectiveness and relative worth of each of the studied technologies are summarized and compared in terms of the resulting sludge properties, the digester performance, the environmental benefits and the current state of real-world application. The challenge and technical issues encountered during sludge cotreatment are discussed, and the future research needs in promoting full-scale implementations of those approaches are proposed.

1. Introduction

Sewage sludge is increasingly produced during wastewater biological treatment process. It contains a myriad of toxic substances such as pathogens, heavy metals and some organic contaminants, which creates odors and hygiene concerns. Improper use and disposal of sewage sludge causes severe environmental impacts and health hazard to the public. The water industry is facing unprecedented economic and environmental constraints because of not only increasingly stringent regulations [1] but large amounts of sewage sludge produced. The disposal of sewage sludge is one of the expensive items in a wastewater treatment plant (WWTP), usually accounting for up to 50% of the total operating costs of the plant [2]. Thus, the promotion of economically feasible treatment methods represents one of the most critical missions for waste management authorities.

Nowadays, there have been several representative techniques for sewage sludge disposal applied in practice, e.g. landfill, compost, drying-incineration, anaerobic digestion, land application and recycling as building materials. Amongst them, anaerobic digestion is of great promise for sewage sludge treatment as it removes odors and pathogens, stabilizes sludge and more importantly, produces renewable energy in the form of methane. This can either cover part of the energy requirements for sewage sludge treatment or, to a certain degree, alleviate human's dependence on fossil fuels. For these reasons, anaerobic sludge digestion reduces the capital costs of a wastewater treatment plant (WWTP) and is deemed as an essential part of a modern WWTP. Anaerobic digestion involves a series of steps, i.e. hydrolysis, acidogenesis (fermentation), acetogenesis and methanogenesis. Many researchers in the literature agree that hydrolysis is the rate-limiting step in sewage sludge anaerobic digestion because of the

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complex floc structure (such as extracellular polymeric substances) and hard cell wall, leading to high retention times, low organic solids degradation and unsatisfactory methane output [3,4]. To accelerate the hydrolysis and enhance subsequent methane productivity, a variety of sludge pretreatment options, such as mechanical, thermal, chemical, biological processes or integrations of these, have been developed at laboratory or pilot level so far with various levels of success [4–7]. If properly designed, pretreatments can facilitate the release of intracellular substances by rupturing the cell wall and make them more accessible to subsequent microbial actions. The favorable characteristics of pretreatment in improving microbial cell lysis, bioavailability, organic solids degradation, methane production, mass reduction and avoidable costs of digestate dewatering have been repeatedly documented.

In the view of the beneficial role in sludge disintegration, pretreatment has gained much more concerns within scientific communities in the past decade, inducing great progresses in both journal publications and the field. The ScienceDirect shows that the number of publications per year with sludge “pretreatment (pre.)” and “anaerobic digestion (AD)” as topics increased sharply: only 36 papers published in 2000, over 100 papers per year since 2006 and up to 609 papers in 2015, with the corresponding percentage of “sludge pre.-AD”-based papers in all papers related to “sludge AD” rising from 24.5% in 2000 into 43.6% in 2015 (Fig. 1). This shows the ever-growing importance of pretreatment played in sewage sludge anaerobic digestion. Pretreatment seems have become an indispensable step nowadays prior to anaerobic digestion of sewage sludge. In the recent past, Carrere et al. [8,9], Pilli et al. [10,11], Cano et al. [12], Le et al. [13], Meyer and Edwards [14], and Joo et al. [15] have made the state of the art overview of most reported pretreatment techniques with unique favor or emphasis so as to evaluate the potentials and effectiveness of pretreatment in accelerating sludge anaerobic digestion.

This review is an attempt to comprehensively review and analyze the relative worth of each pretreatment alternative in terms of principle mechanisms, recent developments, potentials, current state of commercial operations and possible benefits. Recently emerging pretreatments as well as novel approaches are firstly reviewed. Furthermore, the possible technical issues stated in several studies are summarized to critically outline different aspects of pretreatment technologies. In addition, a significant consideration for selecting a pretreatment technology is economic-environmental benefit. Pretreatment has the ability to enhance sludge reduction and methane recovery, but meanwhile leads to additional energy input and greenhouse gas (GHG) emissions. A systematic assessment of different pretreatment technologies for biogas production is quite necessary and imperative for deciding which one would be the most suitable from an industrial point of view. Therefore, this review will also propose a “cost-benefit analytic method” to assess the technical availability of each pretreatment method from the energetic, economic and environmental perspectives of view, with the aims of providing valuable guidelines for their feasibility for further applications on a pilot- and full-scale, and helping the industry to determine the most cost-efficient cotreatment route to ensure the optimal sludge conversion and energy recovery.

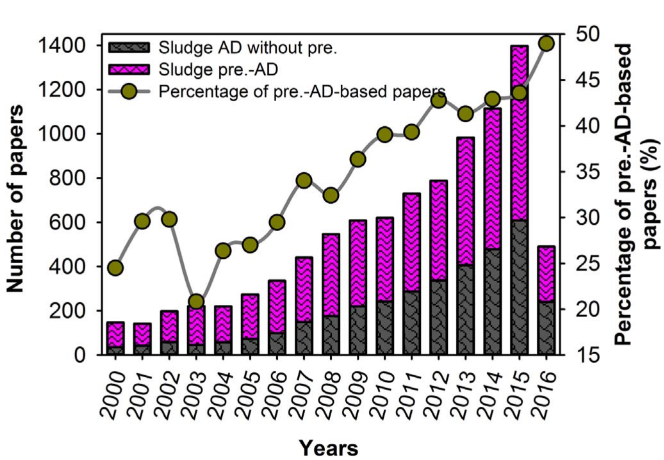

Fig. 1. ScienceDirect bibliometric study with the topics “sludge AD”, or “sludge pre.-AD” (February 2016); sludge AD: sludge “anaerobic digestion” alone; “sludge pre.-AD”: the combination of sludge “pretreatment” with “anaerobic digestion”.

2. Sewage sludge production and anaerobic digestion

2.1. Sewage sludge production

In biological wastewater treatment process, the part of chemical oxygen demands (COD) removed is converted into biosolids, which makes up sewage sludge. Sewage sludge usually represents 1–2% of the treated wastewater volume. As per UN-Habitat's statistics [16], the existing WWTPs in USA, for instance, generate over 6.5 million tons dry solids (Mt DS) annually; it is estimated to be around 3.0 and 2.0 Mt per year produced in China and Japan, respectively (Fig. 2). The figures are naturally anticipated to increase in the near future when considering the growing applications of wastewater treatment plants in developing countries. The main disposal routes and rates are different in different countries, heavily depending upon the economic development level. As illustrated in Fig. 2, in developed countries such as USA the reuse and disposal rate reaches up to 94% and it is roughly 97% in Japan, where more than half (52%) of sewage sludge is being recycled to produce building materials and 12% anaerobically digested for bioenergy recovery. Comparatively, the situation of sewage sludge use and disposal in developing countries is far beyond optimism. For example, in China over 80% of sewage sludge is dumped improperly. Even for landfill, the most commonly used method in China, a majority of sludge is being disposed of directly after mechanical dewatering with higher than 80% moisture content and very low compressive strength. Note that for a sanitary landfill, the threshold of sludge water content is 60% from the view of safety regulations [17]. The simple disposal not only causes the wasting of resources but also brings about a series of secondary disasters (e.g. landslide, environmental pollution, etc.). Sewage sludge management is highly complex and costly, representing a stern global challenge. It is apparent that more efforts devoted to sludge management are still urgently required in developing countries.

2.2. Basic principles of anaerobic digestion

Anaerobic digestion, as stated before, comprises several successive biochemical processes (i.e. hydrolysis, acidogenesis, acetogenesis and methanogenesis) involving different groups of microbes (Fig. 3) [2,19,20]. In the first step, complex organic matters such as proteins, polysaccharides and lipids are solubilized and hydrolyzed into simple soluble components (e.g. amino acids, long-chain fatty acids (LCFAs), sugars and alcohols) under the assistance of extracellular enzymes. Key bacteria involved in hydrolytic phase include *Clostridium*, *Cellulomonas*, *Bacteroides*, *Succinivibrio*, *Prevotella*, *Ruminococcus*, *Fibrobacter*, *Firmicutes*, *Erwinia*, *Acetovibrio*, *Microbispora*, etc. [19,21]. The hydrolyzed molecules in the second step are converted by acidogenic (or fermentative) bacteria such as *Peptoccus*, *Clostridium*, *Lactobacillus*, *Geobacter*, *Bacteroides*, *Eubacterium*, *Phodopseudomonas*, *Desulfovibrio*, *Desulfobacter*, *Sarcina*, etc. [20,22], to short-chain volatile fatty acids (VFAs) and other minor by-products such as ammonia (NH_3), H_2 and CO_2. During acetogenesis process, acetogens further decompose the higher organic acids (e.g. propionic and butyric acids) to form primarily acetic acid, and H_2 via β-oxidation; however, the conversions are only favorable thermodynamically under particularly low concentrations of the reaction products (acetate and H_2) (i.e. acetate concentration: 10^{-4}–10^{-1} mol/L; H_2 partial pressure required for propionate: 10^{-6}–10^{-4} atm; and for butyrate: $(1.0–7.0)\times10^{-3}$ atm) [23,24]. Typical acetogenic bacteria

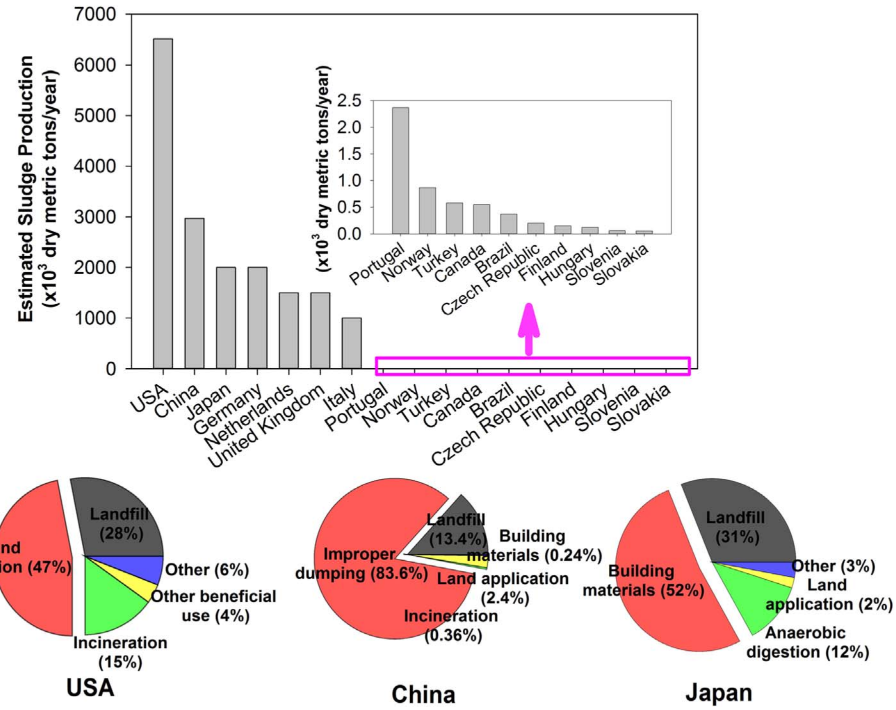

Fig. 2. Estimated sewage sludge production as per the statistics of UN-Habitat [16] and the situation of sewage sludge use and disposal in USA ("U.S. Wastewater Treatment Factsheet." Pub. No. CSS04-14, 2015), China [18] and Japan (Ministry of Land, Infrastructure, Transport and Tourism, Japan), etc.

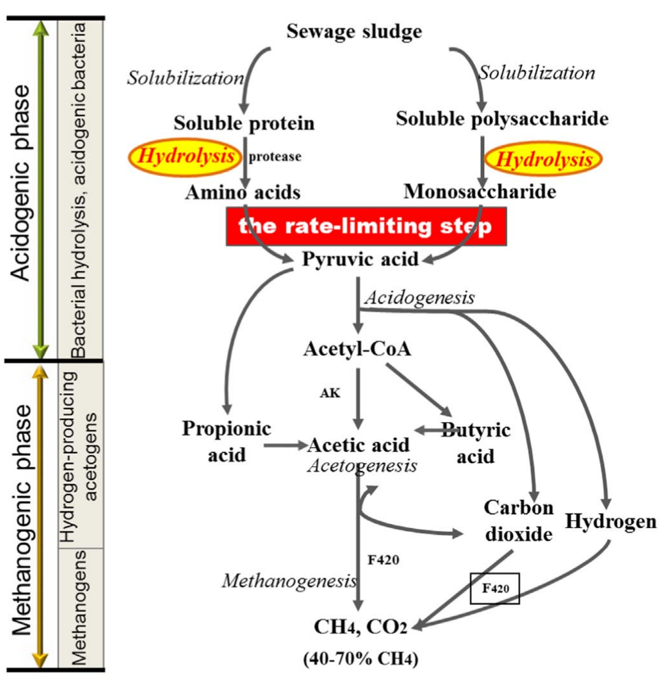

Fig. 3. Proposed metabolic pathway for methane production from sewage sludge anaerobic digestion (modified from Mu and Chen [31].

comprise for example *Syntrophobacter*, *Syntrophus*, *Pelotomaculum*, *Syntrophomonas*, *Syntrophothermus*, *Moorella*, and *Desulfovibrio* [21,25]. Finally, a myriad of methanogenic a*rchaea* metabolize acetate via acetoclastic methanogenesis ($CH_3COOH+H_2O \rightarrow CH_4+H_2CO_3$, $\Delta G^{0'}$ =−31 kJ/mol) with *Methanosarcina* and *Methanosaeta* as the main microbes, as well as the mixture H_2/CO_2 via hydrogenotrophic methanogenesis ($CO_2++4H_2 \rightarrow CH_4++2H_2O$, $\triangle G^{0\prime}$ =−136 kJ/mol) with *Methanobacterium* and *Methanoculleus* being the main organisms to produce methane [26,27]. For a long time, scientists have been agreeing that acetate is the most preferred methanogen substrate, producing 70% of the methane with the remaining 30% from the redox reaction of H_2 and CO_2 [19]. However, the statement is being questioned and challenged when using complex biomass such as energy crops [28], beet silage [29], or maize silage [30] as the feedstocks, in which researchers discovered the predominance of hydrogenotrophic methanogens over acetoclastic methanogens for methane evolution.

2.3. Special features of sewage sludge and "high difficulty with digestion"

Sewage sludge floc is a multiphase medium, and constitutes the vast majority of components including microbial aggregates, filamentous bacterial strains, organic and inorganic particles, extracellular polymeric substances (EPS) and large amount of water [32] (Table 1). The composition of sewage sludge varies, depending upon the type and original components of the raw wastewater. EPS, originating from the microbial activity (secretion and cell lysis) and/or from the wastewater itself, i.e. from the adsorption of organic matter (e.g. cellulose, humic acids, etc.), are the major constituent of sludge organic fraction [33], mainly composed of proteins (PN), polysaccharides (PS), nucleic acids, humic substances, lipids, etc. Depending on the spatial distribution within sludge floc matrixes, EPS are usually divided into three categories: slime EPS (S-EPS), loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS). S-EPS are evenly distributed in the aqueous phase and LB-EPS extend from TB-EPS and are characterized by a highly porous and dispersible structure; comparatively, TB-EPS adhere to the surface of the bacterial cells inside the sludge flocs [34,35]. The presence of these three-dimensional, gel-like and negatively charged biopolymers govern the surface physicochemical properties of sludge matrixes [36]. EPS provide the protective shielding and prevent the cell rupture and lysis, thereby influencing sludge functional integrity, strength, flocculation, dewaterability and even biodegradability. Besides the protection from EPS, microbial cells themselves possess a hard cell envelope composed of glycan strands crosslinked by peptide that presents physical and chemical barriers to direct anaerobic digestion. In consequence, the sewage sludge with high EPS and cells content has the stiff structure and will be more difficult to hydrolyze

Table 1
Basic characteristics of different sludge types: primary, activated, mesophilic anaerobically digested and thermophilic anaerobically digested sludge (adopted from [36]).

Parameters	Primary sludge	Activated sludge	Mesophilic	Thermophilic
VSS/SS	0.77 ± 0.07	0.75 ± 0.05	0.60 ± 0.02	0.67 ± 0.11
Proteins (mg/g SS)	140 ± 6	346 ± 111	248 ± 12	155 ± 62
Polysaccharides (mg/g SS)	198 ± 93	101 ± 35	70 ± 5	78 ± 10
Humics (mg/g SS)	80 ± 55	58 ± 35	112 ± 108	188 ± 92
Total EPS (mg/g SS)	75 ± 55	130 ± 65	78 ± 49	41 ± 9
EPS proteins (mg/g SS)	33 ± 9	76 ± 32	40 ± 7	20 ± 12
EPS polysaccharides (mg/g SS)	5.0 ± 2.3	11.9 ± 4.5	6.5 ± 2.0	5.9 ± 1.3
EPS humics (mg/g SS)	36 ± 46	42 ± 39	31 ± 44	15 ± 5
Fe (mg/L)	71 ± 71	212 ± 172	202 ± 53	158 ± 91
Ca (mg/L)	235 ± 215	362 ± 575	801 ± 792	139 ± 167
EPS surface charge (meq/g SS)	0.18 ± 0.24	0.33 ± 0.29	0.21 ± 0.23	0.08 ± 0.05
Zeta-potential (mV)	−35	−29.6 ± 8.5	−30.7 ± 10.5	−26.5 ± 4.4
Sludge surface charge (meq/g SS)	0.21	0.13 ± 0.07	0.17 ± 0.12	0.17 ± 0.18
Floc size (μm)	53	125 ± 109	51 ± 21	57 ± 11
Shear sensitivity k_{SS}	0.125	0.062 ± 0.049	0.244 ± 0.016	0.418 ± 0.337
Surface area C_S (m^2/g SS)	21.8	15.6 ± 8.6	66.3	–

and digest. This explains the low overall volatile solids (VS) destruction efficiency (30–50%) of raw sludge in conventional mesophilic anaerobic digesters even at very long retention time of 20–30 d [2].

3. Pretreatment of sewage sludge to improve anaerobic biodegradability

The complex microstructure and components make sewage sludge especially difficult to hydrolyze. Owing to the high resistance of sludge to biodegradation, pretreatments are often adopted before undergoing anaerobic digestion. The main goal of pretreatment is to disrupt EPS matrix and cell wall and to make the available nutrients accessible to microbes thus speeding up the conversion of organic solids and methane productivity. In this section, five approaches including mechanical, thermal, chemical, biological as well as several combination of different processes are briefly reviewed.

3.1. Mechanical pretreatment

3.1.1. Ultrasonic pretreatment

Ultrasonication is a well-established mechanical technology for sludge disintegration. Ultrasound waves cause the periodical compression and rarefaction when propagating through the medium [37,38] (Fig. 4a). The microbubbles formed during this process violently collapse within a few microseconds after reaching a critical size, inducing the occurrence of cavitation. The sudden and violent collapse leads to extreme conditions (a local temperature of around 5000 K and a pressure above 500 bars) [39] and initiates powerful hydro-mechanical shear forces and highly reactive radicals (H• and •OH). Both the hydro-mechanical shear forces and the oxidizing effect of H• and •OH contribute to the break-up of sludge flocs and the liberation of intercellular material. In comparison, hydro-mechanical shear forces nonetheless is stronger in sludge rupture than radicals. More detailed descriptions of the method are provided in Pilli et al. [10] and Le et al. [13].

Low-frequency (20–40 kHz) ultrasound, first applied in lab-scale cell lysis study in the 1960s, has been frequently adopted on lab, pilot and full-scale level to sludge disintegration [40,41] (Table 2). Martín et al. [42] reported that ultrasonication effectively improved anaerobic digestion of sewage sludge. Methane yield of sewage sludge after ultrasonication pretreatment increased from 88 to 172 mL STP/g VS, increasing by around 95%. The biodegradability of pretreated sewage sludge reached 81% in VS, which gave a maximum OLR of 4.1 kg VS/m^3 d and a methane production rate of 1270 L STP/m^3 d. Sludge solubilization efficiency relies on specific energy (SE) input (SE = $\frac{P_{US} \times t}{V \times TS}$, J/kg TS) [43]. For complete disaggregation of sludge flocs around 80 kJ/L is required, while for the damage and death of the released free cells, higher levels need to be applied [44]. The threshold of specific energy usually reported in literature is between 1000 and 16,000 kJ/kg TS [8,9]. For instance, Feng et al. [43] investigated the effect of ultrasound the physical-chemical characteristics of sludge and confirmed that a SE of 1000 kJ/kg TS may be the optimal energy for improving sludge settleability while for sludge disintegration and solubilization, a SE dose >5000 kJ/kg TS should be poised. Further increase in the applied SE to 26,000 kJ/kg TS contributes more to the destruction of sludge flocs and the transformation of insoluble organics into soluble form, but it exhausts much higher energy. In order to reduce energy consumption, in the case of Chu et al. [39], they used "weak" ultrasonic pretreatment at 20 kHz and 0.33 W/mL for 20 min to enhance waste activated sludge anaerobic digestion, which affected a 104% increase in ultimate methane yield from 143 to 292 g CH_4/kg DS. Notwithstanding less efficient release of insolubles into the suspension, insufficient ultrasound dose allows the organics to be more easily attacked by the hydrolyzed enzyme. It is worth noting that for a given specific energy, higher power was more efficient than a longer treatment time but lower power [45]. It is reported that ultrawave system has at least 20 full-scale and 17 pilot-scale installations for the pretreatment of sludge, mostly in Germany. These ultrasound installations may result in a 15–35% increase in volatile solids destruction and a 15–35% increase in biogas production [46].

Besides the use in sewage sludge anaerobic digestion, ultrasound also has been used for enhancing sludge dewaterability [47,48]. For example, Feng and co-workers [49] found that the optimal specific energy to give maximal dewaterability characteristics was 800 kJ/kg TS, which generated sludge with optimal EPS concentration (400–500 mg/L) and particle size distribution (80–90 microm diameter).

3.1.2. Microwave irradiation

Like ultrasonication, microwave (MW) irradiation is considered as a popular alternative to the conditional heating (CH) technology. In the electromagnetic spectrum, MW irradiation operates in wavelengths of 1 mm–1 m with corresponding oscillation frequencies 0.3–300 GHz [37,66]. In industry, a shorter frequency either close to 900 MHz or at 2450 MHz is often adopted [68]. Damages to sludge cells with MW irradiation may occur in two ways (Fig. 4b): (i) thermal effect that is generated through the rotation of dipoles under oscillating electromagnetic fields, which heats the intracellular liquor to boiling point and brings out the break-up of bacterial cells [69]; and (ii) athermal effect that is induced by the changing dipole orientation of polar molecules, giving rise to the possible breakage of hydrogen bonds and unfolding and denaturing of complex biological molecules [70], which kills

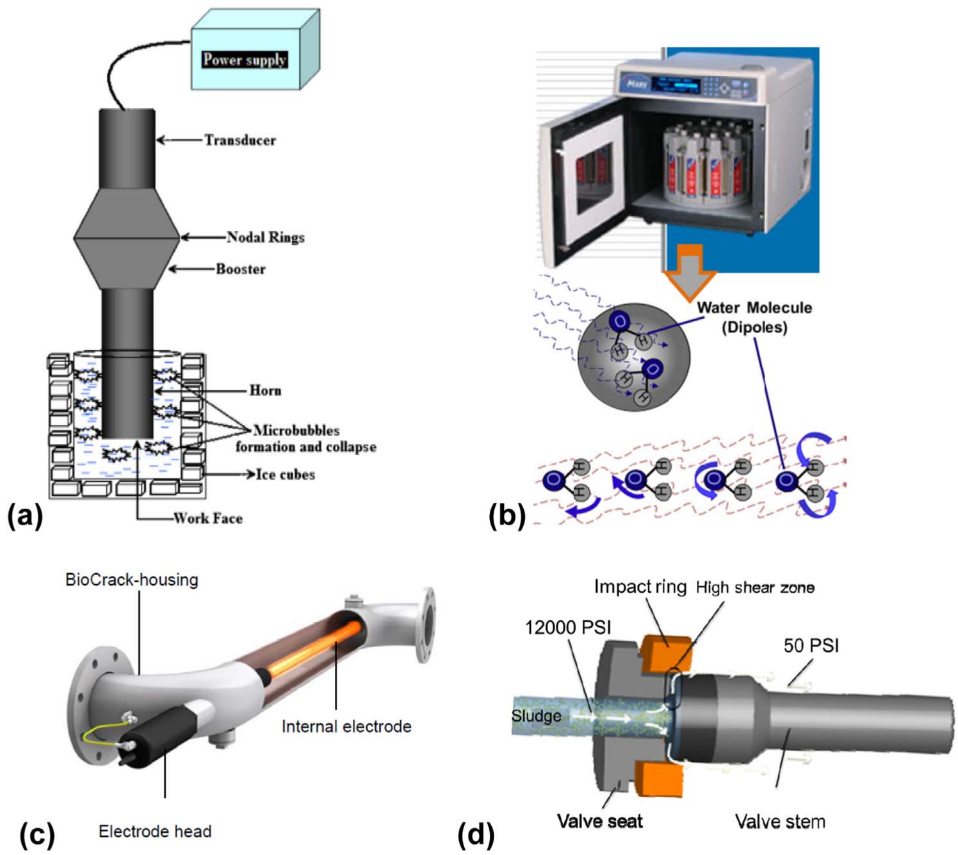

Fig. 4. Configurations of ultrasonication [10] (a), microwave irradiation [63,64] (b), electrokinetic disintegration (the BioCrack module, http://www.engineered-to-work.com/web/infomaterialien/biocrack_bga_ka_en.pdf) (c) and high-pressure homogenizer (HPH) (the MicroSludge™ module) [65] (d).

microorganisms at lower temperatures.

Previous investigations have verified that MW irradiation is applicable in sewage sludge disintegration before anaerobic digestion with high efficiency [71,72] (Table 2). Appels et al. [55] studied the influence of microwave pre-treatment on sludge solubilization and pilot scale semi-continuous anaerobic digestion and they found that microwave pre-treatment resulted in an effective solubilization of the organic matter in the sludge and a 50% increase in biogas production. Beszedes et al. [73] concluded that MW pretreatment of food industrial sewage sludge resulted in 3.1-fold higher solubility and 1.7-fold increased biogas production. Ahn et al. [74] reported that the solubilization degree (SCOD/TCOD) of sludge increased from 2% (control) to 22% and the biochemical acidogenic potentials increased from 3.58 to 4.77 g COD/L after MW pretreatment (2450 MHz, 700 W for 15 min). Applying MW irradiation (175 °C) to pretreat sewage sludge, Eskicioglu et al. [75] observed 35 ± 1% and 31 ± 6% improvement in solubilization degree and biogas production, respectively. The intensive MW irradiation leads to the rapid disruption of EPS and simultaneous lysis of residue cells of sludge.

Nevertheless, there are conflicting conclusions on the athermal effect of MW irradiation in the literature. Eskicioglu et al. [65] pretreated WAS by MW and CH under identical heating profiles to study the athermal effect of MW; the results indicated that although MW athermal effect did not exert discernable effect on the COD solubilization, it substantially upgraded the mesophilic anaerobic biodegradability of activated sludge and biogas production. In contrast to this study, Mehdizadeh et al. [76] compared the influence of MW (2.45 GHz, 1200 W) and CH pretreatments to dewatered sludge solubilization and anaerobic digestion. It is reported that heating method (CH versus MW) had no statistically significant effect (p >0.05) on biosolids solubilization and methane production. There was no pattern of microwave heated digesters showing enhanced performance over conventionally heated digesters due to the athermal effect. This creates the need for more efforts to determine whether and/or to what extent the athermal effect influences sludge physicochemical characteristics as well as biodegradability.

In addition to the improvement in methane recovery pretreatment with microwaves can also effectively destruct the pathogen present in sludge. A work conducted by Hong et al. [77], for instance, reported ≥2.66 log removal of fecal coliforms that was achieved by the anaerobic digester fed with irradiated sludge with 2450 MHz microwaves. Likewise, Kuglarz et al. [78] confirmed that single microwave pretreatment resulted in 50% reduction of *C. perfringens* while the quantity of *C. perfringens* present in the digested sludge without MW pretreatment was almost the same as in raw sludge. Additionally, several lines of evidences also confirmed the favorable potential of MW irradiation in improving dewaterability of digested sludge [75,79].

3.1.3. Electrokinetic disintegration

Electrokinetic disintegration (or pulsed electric field) is one of the high-voltage electric field methods [80]. During disintegration process, the charges created by the high-voltage field induce the sudden disruption of rigid sludge flocs and cellular membranes, thereby making the nutrients easily available to the fermenting bacteria (Table 2). Lee and Rittmann [61] achieved 110–460% increase in soluble compounds (NH_3-N, VFAs, sugar, and protein) after electrokinetic treatment at a specific energy input of ~34 kWh/m^3, which provoked 33% and 18% increase in CH_4 production and TCOD removal, respectively, in an anaerobic CSTR with a SRT of 20 d. In particular, the electrokinetic treatment saved 40% digester size with a CH_4 conversion of 0.23 g CH_4-COD/g COD. According to Choi et al. [58], electrokinetic disintegration of activated sludge resulted in 4.5 times increase in SCOD/TCOD ratio and 2.5 times higher biogas production at 19 kV, 110 Hz for 1.5 s

Table 2
Summary of typical studies of mechanical pretreatments on sludge solubilization and subsequent anaerobic digestion.

Type of sludge	Pretreatment		Anaerobic digestion		References
	Conditions	Effects	Conditions	Performances	
(a) *Ultrasonication*					
Activated sludge (35.5 ± 0.7 g TS/L)	3380 kJ/kg TS	DD_{COD}: 21%	TPAD-BMP assay (55 °C→35 °C)	>+42% methane production, +13% VS removal	[50]
Secondary sludge (31.4 g TS/L)	20 kHz, 750 W, 5742 kJ/kg TS	Increase of SCOD/TCOD from 0.02 to 0.10	Batch, 35 °C, 30 d	+16.9% VS removal,+7.89 $\times10^{-6}$ kWh/g energy output, 1.0 energy ratio	[51]
Activated sludge (23 g TS/L)	24 kHz, 300 W, ~5000 kJ/kg TS	DD_{COD}: 9%	Semi-continuous, 37 °C, HRT 20 d, 80 d	+35% methane yield, 0.86 energy ratio	[52]
Mixed sludge (132 ± 1 g TS/kg)	150 W, 45 min	Increase of TOC: 81.5%, increase of TN: 50.0%	Batch, 35 °C, OLR 0.9 ± 0.1 kg VS/m^3 d	+95% methane yield	[42]
Thickened sludge (43.6 g TS/kg)	100 W, 8 min, 96 kJ/kg TS	Increase of SCOD: 1741%	Semi-continuous, 37 °C, HRT 20 d, 67 d	+27% biogas production	[7]
(b) *Microwave*					
Activated sludge (14.2 ± 0.7 g TS/kg)	14,000 kJ/kg TS	Increase of SCOD/TCOD from 2% to 21%	Batch, 35 °C, 35 d	+570.7% biogas production	[53]
Dairy activated sludge (11.66 g TS/L)	2450 MHz, 900 W, 12 min, 1814 kJ/L	Increase of SCOD: 19%	Semi-continuous, 37 °C, SRT 15 d, 170 d	+57% biogas production, +64% VS removal	[54]
Thickened sludge (43.6 g TS/kg)	2.45 GHz, 800 W, 1 min, 96 kJ/kg TS	Increase of SCOD: 117%	Semi-continuous, 37 °C, HRT 20 d, 67 d	+ 20%biogas production	[7]
Activated sludge (40.8 g TS/kg)	800 W, 3.5 min, 336 kJ/kg TS	Increase of SCOD: 214%	Semi-continuous, 37 °C, SRT 20 d, 42 d	+50% biogas production, +66.6% DS removal	[55]
Thickened sludge	1250 W, 2450 MHz, 100% intensity	Increase of SCOD/TCOD from 0.06 to 0.2	Semi-continuous TPAD	+106% biogas production, the maximum VS removal: 53.1%, eliminating pathogens and enhancing sludge dewaterability	[56]
(c) *Electrokinetic disintegration*					
Activated sludge	10 kWh/m^3	Increase of SCOD/TCOD to 10%, increase of SCOD from 20 to >1000 mg/L	Batch, 25–30 d	+100% methane production	[57]
Activated sludge	19 kV, 110 Hz, 1.5 s	Increase of SCOD/TCOD: 4.5 times, increase of exocelluar polymers: 6.5 times	Batch, 35 °C, 20–30 d	+2.5 times higher biogas production	[58]
Mixed sludge		Increase of SCOD: 160%, increase of DOC: 120%	Full-scale WWTP	+40% biogas production, biosolids requiring disposal reduced by 30%	[59]
Primary sludge	33 kWh/m^3	Accumulation of acetate increased by 2.6-fold	MEC, anode potential: −0.3 V vs Ag/AgCl	+2.4-fold current density (~3.1 A/m^2)	[60]
Activated sludge	~34 kWh/m^3	Increase of SCOD: 220%	CSTRs, 37 ± 1 °C, SRT 20 d	+33% methane production, +18% TCOD removal, −40% digester size	[61]
(d) *High-pressure homogenization (HPH)*					
Mixed sludge	12,000 psi, 0.009 g NaOH/g TS	SCOD/TCOD: > 4.0	2TPAD, SRT 14 d, OLR 1.24 ± 0.05 g VS/L d	0.61–1.32 L CH_4/L d methane production, 43–64% VS removal, pathogen removal, net energy output	[62]
Sewage sludge (23 g TS/L)	50 MPa, 2 cycles	SCOD: 2167 mg/L, DD_{COD}: 7.7%	Batch, 35 °C, 7 d	+115% biogas production, +41.17% VS removal, +61.89% TCOD removal	[63]
Concentrated sludge (40 g/L)	150 bar, flow rate 2.7 m^3/h		Full-scale, 36–38 °C	+30% biogas production, +23% sludge reduction	[64]

DD_{COD}: sludge disintegration degree ($DD_{COD}=\frac{SCOD_{pre.}-SCOD_0}{TCOD-SCOD_0}$); SCOD: soluble chemical oxygen demand; TCOD: total chemical oxygen demand; TPAD: temperature-phased anaerobic digestion; BMP: biochemical methane potential; HRT: hydraulic retention time; OLR: organic loading rate; WWTP: wastewater treatment plant; MEC: microbial electrochemical cell.

Electrokinetic disintegration, as a newly developed sludge pretreatment technology, has been implemented extensively in industry. For example, a full-scale installation in a WWTP sludge digestion has been described by Rittmann et al. [59]. Electrokinetic pretreatment of 63% of the input waste sludge increased biogas production by over 40% and reduced the biosolids requiring disposal by 30%. They further estimated that for a plant treating 76,000 m^3/d of wastewater (380 m^3-sludge/d), electrokinetic treatment generated an annual economic benefit of approximately $540,000 net of electricity and other operating and maintenance costs. Most recently, Chiavola et al. [81] applied the electrokinetic disintegration in a full-scale WWTP for sludge reduction. The electro-kinetic disintegration was able to drastically reduce the amount of biological sludge produced by the plant, without affecting its treatment efficiency, which gave rise to a considerable net cost saving for the company. In another full-scale implementation at the Northwest Water Reclamation Plant (NWWRP) in Mesa, Ariz., it similarly confirmed the net positive economic benefit as a result of the energy offsets from the increase in biogas (60%) and reduction in biosolids disposal (40%) [46]. Besides, German Vogelsang is one of the representative electrokinetic disintegration device producers (called as "BioCrack module"). The BioCrack module is composed of a system of pipes with alongside electrodes that applied a voltage of around 30–100 kV (Fig. 4c). The company claims that the application of BioCrack module to pretreat sludge increases biogas yields by up to 20% at poised power 35 W per module while offering roughly 30% downstream energy savings (pumping, mixing, etc).

3.1.4. High-pressure homogenization

The major principle of high-pressure homogenization (HPH) relies on abrupt pressure gradient, high turbulence, cavitation as well as strong shearing forces, which are aroused under strong depressurization of highly compressed sludge suspensions (up to 900 bar) [8] (Fig. 4d). During this process, sludge flocs break and cell membrane ruptures releasing the intracellular substances. Hence, HPH can bring improvement in sludge disintegration and biodegradation performance.

There are many lab-scale investigations or full-scale demonstrations nowadays reporting the effect of HPH pretreatment on sludge solubilization and biogas production (Table 2). Zhang et al. [82] investigated the effects of homogenization pressure (20–80 MPa) and homogenization cycle (1–4) on sludge solubilization. The increase of homogenization pressure from 20 to 80 MPa or homogenization cycle from 1 to 4 was favorable to sludge solubilization. HPH treatment at 30 MPa with one homogenization cycle for the sludge sample with a TS of 2.48% was the most energy-efficient. Rai et al. [83] also observed that sludge DD_{COD} increased to 4.5%, 10.7% and 12.5% at 200, 300 and 400 bar treatments, respectively; however, there was no further improvement for higher homogenization pressure. In a lab-scale semi-continuous experiment, Wahidunnabi et al. [62] compared two-phased anaerobic digestion (2PAD) with HPH pretreatment (HPH++2PAD) to conventional anaerobic digestion (i.e. single-stage (control) and 2PAD) of municipal sludge. Homogenizing pressure was found as the most significant factor (p <0.05) affecting solubilization of particulate COD and biopolymers in sludge. At 12,000 psi and 0.009 g NaOH/g TS, HPH++2PAD system achieved the maximum methane production (0.61–1.32 L CH_4/L digester-d) and VS removals (43–64%), as well as significant pathogen removals and positive energy balance. HPH option is characterized by easy operation, low investment, and high energy-efficiency and accordingly has been in high popularity in large-scale implementations over the past years. In a demonstration project as described by Onyeche [64], a modified homogenizer at 150 bar with flow rate of 2.7 m^3/h was employed to pretreat concentrated sludge; the results indicated about 23% sludge reduction with more than 30% increased biogas production, leading to enormous savings in sludge disposal costs. Besides, Rabinowitz and Stephenson [67] applied a patented MicroSludge™ unit in a demonstration project in Los Angeles WWTP in October 2005. The process uses chemical pre-treatment to weaken cell membranes and a HPH to burst the cells.

3.2. Thermal hydrolysis

Thermal hydrolysis (TH) is a well-established and commercially implemented pretreatment technology that, originally used to enhance sludge dewaterability [84,85], has been extensively studied in an effort to improve digestibility of sewage sludge (Table 3). Some of these efforts have been well documented recently in detail [86,87]. The performance of the TH process heavily relies upon treatment temperature and time used. In the early 1990s, Li and Noike [88] investigated the effect of TH temperature (62–175 °C) and time (15–60 min) on the biological degradation of waste activated sludge in batch and continuous experiments. They observed that sludge solubilization increased with increasing temperature and the TH effect impacted more on carbohydrates and proteins than on lipids. For an anaerobic sludge treatment system comprised of TH, the optimal temperature for TH was 170 °C under treatment time of 30–60 min, reducing SRT by 5 d and increasing biogas production. No inhibitory effect appeared at the temperature studied. Hereafter, TH pretreatment of sludge has increasingly drawn the attention of environmental researchers at large. Carrère and co-workers [89] applied TH process (60–210 °C) to pretreat six different waste sludges and found that sludge solubilization increased with treatment temperature up to 190 °C. In the studied temperature range, biodegradability enhancement or methane production increase by thermal hydrolysis showed a function of sludge COD solubilization. Further increasing TH temperature (i.e. to 210 °C) reversely weakened biodegradability. They attributed this to the formation of recalcitrant compounds in the Maillard reactions, i.e. melanoidins (high-molecular-weight heterogeneous polymers) which are particularly difficult to degrade and even inhibit the biodegradation of other organics [90]. They further concluded that thermal treatment time had less impact on sludge solubilization in comparison with temperature. Sludge solubilization did not seem to be different even if its treatment was longer (4 h vs. 30 min). On contrary, if temperatures are not high enough, hours to several days of heating period may be required [91]. Kinnunen et al. [92] investigated the effect of thermal pretreatments on the solubility and methane production of nine paper biosludge (2 h at 80 °C, 20 min at 105 °C, 121 °C, or 134 °C). Thermal pretreatments at 105–134 °C increased biosludge solubility and enhanced the BMP by 39–88% while pretreatment at 80 °C did not affect the final BMP; in continuous mesophilic anaerobic process, thermal pretreatment at 121 °C increased methane yield by 77% (138 NL CH_4/kg VS), shortening HRT to 10 d (OLR 2.2 kg VS/m^3 d), while the digestion of the untreated biosludge failed with 10-d HRT due to slow hydrolysis. Shorter HRT enables smaller reactor size, decreasing energy consumption. In the case of Climent et al. [90], they documented that the TH time for secondary sludge when pretreated at 70 °C reached up to 9 h. In another study coupling TH with mesophilic anaerobic digestion, Xue et al. [93] noted that in contrast to low-temperature TH (60–90 °C), high-temperature TH (120–160 °C) accelerated the digestion rate and increased the biogas yield of high solid sludge while simultaneously reducing SRT from 18 to 20 to 12–14 d. In consequence, most of the studies in literature agree that the optimal conditions for TH pretreatment are temperatures of 160–180 °C and time in the range 30–60 min [88,94]. The major benefits of TH pretreatment include pathogens destruction, odor removal, reduction of sludge volume, improved dewaterability with subsequent enhancement of sludge handling as well as positive energy balance [9,95].

Owing to the inherent advantages, several kinds of full-scale TH processes such as CambiTHP™ and Biothelys® have been commercialized world-wild. The main operating parameters are 150–165 °C, 20–30 min, 8–9 bar for CAMBI, and 165 °C, 30 min, 9 bar for BIOTHELYS [87,96]. Fig. 5 illustrates the TH flow diagrams of CambiTHP™ and Biothelys®. The CambiTHP™ is a proven and reliable process that has been used in projects around the world since 1995. The main merits of this patented technology, as provided in Cambi homepage, include: (i) increased sludge bio-degradability and biogas production, (ii) significant sludge cake volume reduction, (iii) 2–3 times increase in digester capacity, (iv) eliminated foaming problems, (v) improved sludge dewaterability (up to 40% dry solids after being dewatered) and (vi) pathogen-free bio-solids (class A) with no regrowth or reactivation of bacteria. The performances of CambiTHP™ process installed in several countries are given on the web site http://www.cambi.com/References. With 51 plants worldwide ranging from 1200 to 135,000 t DS/year committed to the CambiTHP™ process, and 19 countries adopting CambiTHP™ process. The Biothelys® TH process was originally developed by Veolia in the late 1990s. A number of full-scale Biothelys® TH plants with throughputs of between 1000 and 32,000 t DS/year were built in France, Italy, UK, etc., from 2006 to 2013, which fully demonstrated the capabilities and reliability of the process [96].

Table 3
Summary of typical studies of thermal and chemical pretreatments on sludge solubilization and subsequent anaerobic digestion.

Type of sludge	Pretreatment		Anaerobic digestion		References
	Conditions	Effects	Conditions	Performances	
(a) *Thermal hydrolysis*					
Mixed sludge (6% TS)	150–170 °C, 4.80–7.90 bar		Pilot-scale, 37–42 °C, SRT 15–20 d	+24–59% biogas production, increase of VS removal from 50% to 56–62%,+52–92% odor reduction	[95]
Dewatered activated sludge (16% TS)	Pilot-scale CAMBI™, 65 °C, 6 bar, 20 min	Increase of VS removal from 26% to 42% (+62%)	Pilot-scale, treated sludge: primary sludge (80%: 20%), 37 °C, SRT 20 d	+2.3 times increase in SLR,+30–40% biogas production, improved dewaterability	[97]
Secondary sludge (30.00 g TS/L)	134–140 °C, 3.4 bar, 30 min		Batch, 35 °C, HRT 30 d	+40.2% methane production,+12.6% VS removal,+6.8% digestate reduction	[98]
Dewatered sludge (16.7 ± 0.5% TS)	140–160 °C, 60–90 min	Increase of DD_{COD} from 4.5% to 34.7–42.5% (+6.7–8.4 times)	Batch, 37 °C, 28 d	+~16.5% biogas production, reduction of SRT from 18 to 20 d to 12–14 d	[93]
Dewatered sludge (15–20% TS)	Full-scale CAMBI™, 160 °C, 6 bar	SS removal: 20–30%, increase of SCOD/TCOD from 0.04 to 0.4	Semi-continuous, 42 and 55 °C, HRT 1–6 d, 142 d	+2–5 times in VFAs yield,+4–6 times in VFA production rate	[99]
(b) *Chemical*					
Activated sludge (5% TS)	8.75 mL HCl/kg wet sludge, pH 2	4 and 6 times increase of soluble carbohydrates and proteins, respectively	Semi-continuous, 35 °C, HRT 12 d	+14.3% methane yield, −40% polymer dose for dewatering	[100]
Anaerobically digested sludge	170 °C, pH 5–6 (H_2SO_4), 1 h		Continuous, 35 °C, HRT 20 d	+2–2.5 times VSS removal,+14–21% methane production, 22–23% better dewaterability	[101]
Activated sludge	130 °C, pH 10 (KOH)	DD_{COD}: around 60%	Continuous, 35 °C, HRT 20 d	+36.4% COD removal,+33% TS removal,+74% biogas production	[102]
Pulp and paper sludge	8 g NaOH/100 g TS	Increase of SCOD: 83%, 56–192% higher SV	Batch, 37 °C, 42 d	1040 mg acetate/L,+83% methane yield (0.32 m^3 CH_4/kg $S_{removed}$); sodium toxicity at 16 g NaOH/100 g TS	[103]
Activated sludge (10.6 ± 0.1 g TS/L)	pH 9–11 (4 mol/L NaOH), 24 h		Batch, 37.0 ± 0.1 °C, 25 d	+10.7–13.1% TSS removal,+6.5–12.8% VSS removal,+7.2–15.4% biogas yield, improved dewaterability	[104]
Sewage sludge	0.1 mol NaOH/L	Increase of DD_{COD} from 22.3% to 26.9%	Batch (BMP), 21 d	+26.4% organic removal,+1.5% biogas yield; delay of anaerobic digestion start up due to residual NaOH	[105]
Activated sludge (11.7 ± 2.3 g TS/L)	8 g NaOH/m^3 wet sludge (pH 8)	SCOD/TCOD: 1.99%	CSTR, 55 °C, HRT 21 d	+9.7% TS removal,+11.5% VS removal,+18.1% COD removal, 84.22–78.24 mL/d for biogas (−7.1%)	[106]
Sewage sludge	0.1 g O_3/g COD	Oxidization of organics: 38%, solubilization of organics: 29%	Batch, 33 °C, 30 d	+1.8 times methane yield,+2.2 times production rate, decreased dewaterability	[107]
Maize canning sludge	~0.18 g O_3/g DS	Increase of BOD_5/COD from 26% to 93% (+2.58 times)	Batch, 30 °C, 30 d	Increase of biogas production from 1.037 to 9.52 cm^3/g COD d (+8.2 times)	[108]
Activated sludge	10 mg O_3/g TSS, 20 cycles, 30 s/cycle	DD_{COD}: 18%, VSS reduction: 18%	Batch, F/I 0.8, 35 °C, 20 d	+800% specific biogas production, +1.6 folds VSS reduction	[109]
Activated sludge	0.09 g O_3/g MLSS, pH 11	COD solubilization: 40%, TS reduction: 30%	Lab-scale AS-MBR, 120 d	Solids degradation: 37%	[110]
Activated sludge (13.9 ± 0.2 g TS/L)	50 mg H_2O_2/g TS, 7 mg Fe/g TS in sludge, pH 2.0,	Increase of SCOD from 8 ± 1 in control to 103 ± 7 mg/g TS (+11.9 times)	BMP, 37 ± 1 °C, 23 d	+10% methane production,+13% methane potential but no significant effect on hydrolysis rate (estimated	[111]

(continued on next page)

Table 3 (*continued*)

Type of sludge	Pretreatment		Anaerobic digestion		References
	Conditions	Effects	Conditions	Performances	
	30 min			via the first-order kinetic model)	
Activated sludge (10.2 mg TS/L)	4 g $Fe^{2+/0}$/ kg TS, 40 g H_2O_2/kg TS, pH 3, 1 h	DD_{COD}: 23.6% (Fe^{2+}), DD_{COD}: 16.7% (Fe^0)	BMP, 35 °C, 60 d	+30.2% biogas and+38.0% methane production for Fe^{2+},+24.4% biogas and+26.8% methane production for Fe^0	[112]
Secondary wastewater sludge	60 g H_2O_2/kg TS, 0.07 g Fe^{2+}/g H_2O_2, pH 3	Reduction of SS: 21%, reduction of VSS: 25%, increase of SCOD from 0.82 to 7.8 g/L	Lab-scale, 35 °C, 30 d	Increase of methane production from 430 to 496 m^3 CH_4/Mg $VS_{degraded}$,+3.1 times increased net energy, reduced GHG emissions (0.128 Mg CO_2/Mg of TDS)	[113]

SLR: solids loading rate; SV: settling velocity; AS-MBR: aerobic submerged membrane bioreactor; GHG: greenhouse gas; Mg: mega gram, TDS: total dry solids.

The Biothelys® TH process offers better performance relative to the conventional anaerobic digestion system, such as 25–35% less dry matter, 30–50% more biogas production, no odors, safe agricultural reuse, etc. (for more detail see http://technomaps.veoliawatertechnologies.com/biothelys/en/references.htm).

3.3. Chemical pretreatment

Chemical pretreatment employs strong reagents to deform the cell wall and membrane, favoring the availability of sludge organic matter for enzymatic attacks. The major reagents employed in the literature include acids, alkali and oxidants (ozonation and peroxidation).

3.3.1. Acidic and alkali pretreatment

Acidic and alkali pretreatment have shown of great promise in biomass solubilization because of their multiple advantages, e.g. a simple device, ease of operation, high methane conversion efficiency and low cost [4]. Acidic hydrolysis is performed using acids such as HCl, H_2SO_4, H_3PO_4 and HNO_3 while alkali pretreatment usually employs several alkaline solutions, inducing NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, CaO and ammonia. The addition of acid or base avoids the necessity of high temperature and thus can be operated at ambient or moderate temperatures [2]. The effectiveness of acidic or alkali pretreatment may vary with the types and characteristics of the studied substrates because of their distinct affinity to organic components. Acidic pretreatment is indicated to be more effective for lignocellulosic biomass. The main reaction that occurs in this process is the hydrolysis of hemicellulose, which releases the monomeric sugars and soluble oligomers from cell wall matrix into the hydrolysate thereby improving the enzymatic digestibility [114]. The method offers good performance in hemicellulose removal but hardly has impact on lignin hydrolysis, and the lignin condensates and precipitates. Besides, it may induce the formation of toxic by-products, such as furfural and hydroxymethyl furfural (HMF), strong inhibitors to microbial fermentation [114]. Other drawbacks associated with acidic method includes great toxicity and strong corrosivity because of extremely low levels of pH, therefore special materials are required for the reactor construction. For instance, for a 14.3% increase in methane yield of waste activated sludge, pH as low as 2 was required [100] (Table 3). Hence, in order to solve the above problem, the integration of acidic-thermal pretreatment has been presented in the literature, e.g. Neyens et al. [115] with thickened sewage sludge, Nielsen et al. [116] with waste activated sludge as well as Takashima and Tanaka [101] with anaerobically digested sludge.

Alkali pretreatment is comparatively suitable for lignin breakdown. The basic principles of the alkali hydrolysis are based on solvation and saponification [117], which induce depolymerization and cleavage of lignin-carbohydrate linkages [8] accordingly rendering the un-easily biodegradable substances more accessible to the extracellular enzyme. In addition, it solubilizes the xylan hemicellulose by saponifying the intermolecular ester bonds (e.g. acetyl and uronic acid substitutions, etc.) [114], though to a less degree than acidic pretreatment. Alkali method gains higher popularity in sludge disintegration before being sent to the digesters when considering its unique benefits in providing additional alkalinity that increases the buffer capacity of systems, specific methanogenic activity and process stability. Table 3 lists the pretreatment conditions and performance improvements in methane production, and the results are relatively encouraging. Amongst the alkaline reagents, NaOH is the most effective in sludge solubilization and enhancing biogas production, with a ranking of efficacy being (NaOH >KOH >$Mg(OH)_2$ and $Ca(OH)_2$) [118,119]. Lin et al. [103] studied the NaOH pretreatment of pulp and paper sludge (8 g NaOH/100 g TS) and reported an 83% increased methane productivity. However, results tend to underline that the alkali-pretreated sludge with overloading NaOH is not compatible with anaerobic biological digestion [9,105,120]. Too high dose of Na^+ might interfere with the

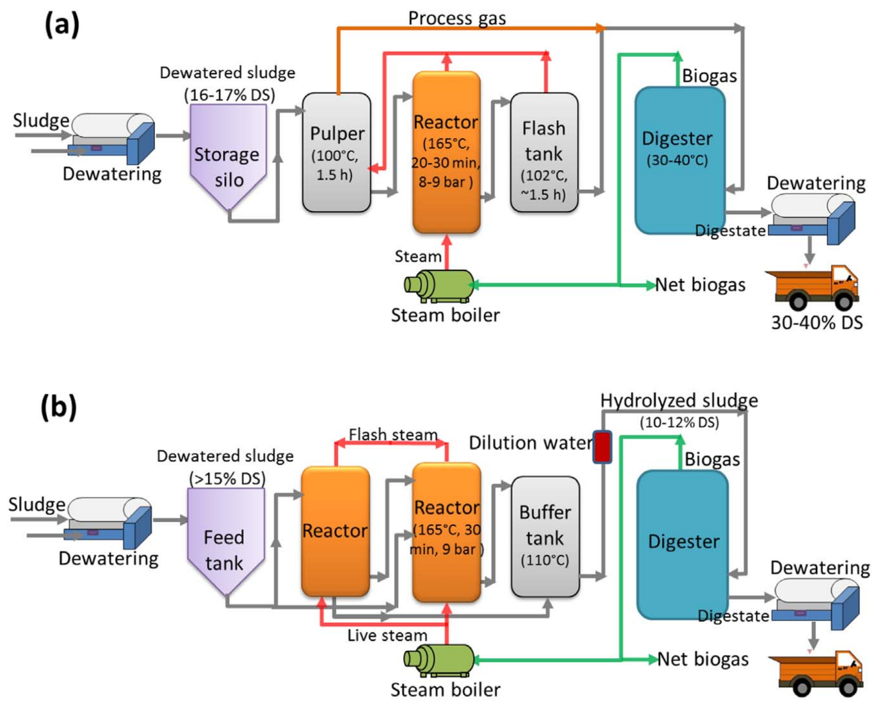

Fig. 5. Thermal hydrolysis process flow diagram: CambiTHP™ (a) and Biothelys® (b).

metabolic pathway of anaerobic microflora and deteriorate methane output [4,105]. Moreover, Penaud et al. [121] attributed the limitation to the formation of refractory molecules as a consequence of pH modifications. Other drawbacks of single alkali hydrolysis include necessity of treated sludge re-neutralization (also for acidic pretreatment) [2], increased mineral content of digested sludge [9], etc.

Of late, alkali pretreatment has been combined with other sludge disintegration methods such as ultrasound [122], microwave [123], thermal [102], HPH [124] and electrolysis [4], with the purpose of reducing alkali consumption and maximizing methane recovery. In addition, alkali conditions (especially pH 10) have also exhibited particularly high attractiveness in promoting sludge fermentation and production of short-chain fatty acids (SCFA), which can be recovered as the organic reactants necessary for biological nutrient removal (BNR) in WWTPs [125–127].

3.3.2. Ozonation

Of the oxidation techniques which have been referred to in the literature, ozonation is the most widely used peroxidation process. It can damage the cell membrane, disintegrate the zoogloea structure and has been successfully put into practice in excess sludge solubilization and reduction [128,129], as well as recirculation of valuable products for improved biological nutrients removal (BNR) in the activated sludge process [130]. In a nitrifying sequencing batch reactor operated in alternating anoxic/aerobic conditions, Dytczak et al. [131] recorded a 14.7% decrease in sludge production and up to 60% improvement in denitrification rate when a pre-ozonation of 0.08 mg O_3/mg TSS was applied. Nie et al. [132] even achieved a zero sludge production system with an ozone dose of 0.1 g O_3/g SS.

Ozonation has been also combined with anaerobic sludge digestion to bypass the hydrolysis step and upgrade biogas production [107,133] (Table 3). Sludge solubilization efficiency is dose-dependent and linearly correlates with the amount of applied ozone in a moderate range [133]. On the other hand, the efficiency of the ozonation process is closely related to both the mass transfer and reaction kinetics of ozone. Kinetic reactions taking place between dissolved ozone and sludge mixed liquor have a lower average rate and as a consequence, in spite of the increase in applied zone dose, it is not possible to observe an ever-increasing COD solubilization [134]. Moreover, too high ozone dose could cause the partial or even complete mineralization of the liberated cellular materials, impacting ultimate methane productivity [9]. The optimal dose of ozone for sludge solubilization varies from 0.05 to 0.5 g O_3/g TS [135], depending on the characteristics of sludge and the pretreatment conditions employed. In addition, sludge ozonation is energy-intensive because it requires high energy for ozone production (12.5 kWh/kg O_3), transfer to the sludge (2.5 kWh/kg O_3) and energy consumption to produce liquid oxygen (0.5 kWh/Nm^3 O_2) [136]. In order to achieve high performances for reducing the costs involved in sludge ozonation, Chu et al. [137] developed a microbubble ozonation process; sludge solubilization efficiency rose from 15–30% for the bubble contactor to 25–40% at ozone doses of 0.06–0.16 g O_3/g TSS, with ozone utilization improving from 72% to 99%. The application of microbubble ozonation accelerates the formation of hydroxyl radicals and speeds up sludge solubilization, thus reducing the impact of high capital requirements. Principles, advantages, drawbacks as well as cost and energy aspects of ozonation process have been described by Chu et al. [130].

Several ozone systems for sludge solubilization and reduction are commercially available, such as (i) Aspal SLUDGE™ (Air Liquide) that offers high solid content of excess sludge, improved dewaterability and low energy consumption; and (ii) Praxair® *Lyso*™ (Praxair Technology, Inc.) that allows up to 80% sludge reduction, 75% reduction in ozone use, as well as an improvement in the settling and dewatering characteristics of sludge.

3.3.3. Fenton oxidation

Another well-established oxidation technology is Fenton process, which involves reactions of hydrogen peroxide (H_2O_2) with catalyst iron ions (Fe^{2+}) to produce highly active hydroxyl radicals (•OH). Hydroxyl radicals have a higher oxidation potential of+2.80 V (in acidic conditions) than hydrogen peroxide (+1.36 V) and ozone (+2.07 V) [11,85] and are particularly effective for the disintegration of sludge EPS and the cell lysis of microorganisms, resulting in the release of both intracellular materials and bound water. In this context, Fenton oxidation has been intensively applied for enhancing sludge dewatering [138–141].

Additional to its application in sludge dewatering, Fenton process enhances biogas production and minimizes sludge weight that needs to be disposed of (Table 3). The effectiveness of this process depends on several variables, namely reagents concentrations (H_2O_2 and Fe^{2+}), Fe^{2+}/H_2O_2 ratio, treatment time as well as initial pH and temperature [85,142]. Dewil et al. [143] proved the effect of Fenton oxidation using 50 g H_2O_2/kg DS and 0.07 g Fe^{2+}/g H_2O_2 at pH 3. This pretreatment improved SCOD by roughly 5.0 times, with 75% higher biogas production over the control. Recently, Pilli et al. [113] treated secondary sludge with 60 g H_2O_2/kg TS, 0.07 g Fe^{2+}/g H_2O_2 and pH 3, at which they noticed 15% increase in methane yield (from 430 to 496 m^3 CH_4/Mg $VS_{degraded}$), 3.1 times increase in net energy as well as considerably reduced GHG emissions (0.128 Mg CO_2/Mg). Furthermore, Sahinkaya et al. [112] investigated and compared the efficiency of conventional Fenton (Fe^{2+}/g H_2O_2, CFP) and Fenton-type (Fe^{o}/g H_2O_2, FTP) processes in sludge disintegration and enhancement of anaerobic biodegradability, and stated that CFP was a more effective process because of using catalyst ferrous iron (Fe^{2+}) in the dissolved form. Under the optimal conditions of 4 g $Fe^{2+/o}$/kg TS, 40 g H_2O_2/kg TS and pH 3 within 1 h oxidation period, CFP and FTP enhanced methane production by 26.9% and 38.0% respectively, relative to the untreated reactor. Also, 10% improvement in methane production was found by Zhou et al. [111] with 50 mg H_2O_2/g TS, 7 mg Fe/g TS and pH 2.0 for 30 min; in this case, the researchers applied indigenous iron in sludge as the catalyst. For more detail of Fenton oxidation in enhancing anaerobic sludge digestion, the reader is referred to Pilli et al. [11]. A major drawback for Fenton reagent is the necessity of low pH values (pH <4.0) [2,144] to avoid hydrolysis and precipitation of Fe^{3+} [138]; moreover, treated sludge needs neutralization before digestion. Apart from this, excess H_2O_2 or Fe^{2+} dose may also scavenge hydroxyl radicals, lowering the concentration of •OH radicals.

3.3.4. Fe(II)-activated persulfate oxidation

Fe(II)-activated persulfate (Fe(II)-$S_2O_8^{2-}$) oxidation is a newly emerging sludge pretreatment technology that was launched firstly by Zhen et al. [35,145] in 2012 to condition and enhance waste sludge dewatering. Persulfate ($S_2O_8^{2-}$) can be activated by heat, UV light or transition metals (Me^{n+}) to generate sulfate free radicals ($SO_4^{-}\cdot$) which are extremely strong oxidants (redox potential 2.60 V). Under the optimal conditions of 1.5 mmol Fe(II)/g VSS, 1.2 mmol $S_2O_8^{2-}$/g VSS and pH 3.0–8.5, this process eliminated capillary suction time (CST) by up to 88.8% within only 1 min. They attributed this to the powerful oxidation and the attack of $SO_4^{-}\cdot$ to EPS and bacterial cells. The $SO_4^{-}\cdot$ destroyed the particular functional groups of fluorescing substances (i.e. aromatic protein-, tryptophan protein-, humic- and fulvic-like substances) in EPS and caused cleavage of linkages in the polymeric backbone and simultaneous destruction of bacterial cells, resulting in the release of EPS-bound water, intracellular materials and water of hydration inside the cells, and subsequent enhancement of dewaterability [35].

Afterwards, Zhen and co-workers further investigated the synergistic effect of Fe(II)-$S_2O_8^{2-}$ oxidation in combination with mild-temperature thermal treatment [146] as well as with electrolysis [147]. Compared to hydroxyl radicals, sulfate radicals own higher oxidation potentials at a wider pH range (3.0–8.5) and are more selective for oxidation at acidic conditions and as a consequence, can be a more cost-effective and alternative approach for improving dewaterability and increasing sludge dry weight from process engineering. Due to the superior features and good performances, Fe(II)-$S_2O_8^{2-}$ oxidation has been attracting unprecedented attention most recently [148–152]. Zero valent iron (Fe^{o}) can also be used as the catalyst in this process [149,153], but its performance may be not comparable to Fe(II) since Fe^{0} needs to dissolve before reaction with $S_2O_8^{2-}$. Unlike in dewatering, to date the literature relation to the application of Fe(II)-$S_2O_8^{2-}$ oxidation in anaerobic sludge digestion is still very scare [154]. Additional research is thus required.

3.4. Biological pretreatment

3.4.1. Temperature phased anaerobic digestion (TPAD)

Biological pretreatment comprises the approaches such as, but not limited to, enzymatic hydrolysis, pre-digestion, as well as the use of fungi or bio-surfactants. Pre-digestion, e.g. temperature phased anaerobic digestion (TPAD) which combines a thermophilic pretreatment unit prior to mesophilic anaerobic digestion (AD), is an effective strategy. The combination of both temperature regimes in TPAD promotes the hydrolysis of feedstocks and acidogenesis in thermophilic range and ensures higher syntrophic acetogenesis and methanogenesis in the subsequent mesophilic stage [155]. As a result, this technology possesses several advantages over single-stage mesophilic digestion process, including higher methane production, better solids destruction, use of low-quality thermal energy, low energy input [156], and sterilization of pathogens [157,158]. There have been a majority of studies evaluating TPAD systems so far. Bolzonella et al. [159] reported the highest specific methane yield of 370 mL/g VS_{added} in TPAD (70 °C, HRT 2–3 d, and 37 °C), 30–50% higher than the mesophilic and thermophilic single-stage tests. Skiadas et al. [160] noted a VS destruction with TPAD system (70 °C, HRT 2 d and 55 °C) of 55% and 43% for primary and secondary sludge respectively, increasing by 43% and 6% than those achieved in the single-stage thermophilic (55 °C) anaerobic digestion. Ge et al. [161] optimized thermophilic pretreatment conditions (temperature, pH and retention time) to improve overall degradability in TPAD and obtained methane production of up to 300 mL/g VS_{added} (HRT 14 d, 35 °C) after thermophilic pretreatment at 1–2 d, pH 6–7 and 65 °C. Besides increasing methane production (0.62 L/g VS), TPAD (55 °C, HRT 3 d, and 35 °C, 15 d) helped obtain Class A biosolids with faecal coliform 10^3 MPN/g TS, and *Salmonella* spp. 1 MPN/4 g TS [162].

In addition, TPAD has been also integrated with other pretreatment methods such as microwave [56], ultrasound [50] prior to thermophilic phase, or ozonation between thermophilic and mesophilic stage [163]. A recent study carried out by Coelho et al. [56] established 10 semi-continuous reactors to test the influence of MW pretreatment, phase separation, digestion temperature and SRT on process performance (Fig. 6). Microwaving coupled with staged digestion enhanced solids destruction, upgraded biogas production, shortened HRT, eliminated pathogens indicators completely, and/or improved dewaterability of digestate. Despite the promising perspectives outlined above, it should be noted that, TPAD process is still in its infancy. Works related to parameter optimization, analysis of energy balance, especially system upscaling, etc. [155], needs to be further conducted before considering its large scale operations. Attention should be also paid to the composition and functional diversity of resident bacterial communities involved in TPAD process, aiming to provide biokinetic parameters for design and optimization of the digesters [164].

3.4.2. Microbial electrolysis cell (MEC)

Microbial electrolysis cell (MEC) that is modified from microbial fuel cell (MFC), is a recent emerging technique for methane production via electromethanogenesis. In a MEC process, exoelectrogenic bacteria in anode consume organic matters anaerobically while releasing electrons to the anode and protons into solution; with a small voltage input, the electrochemically active microorganisms (i.e. electrotrophs) in cathode [165] can accept electrons transferring to cathode through the external circuit [166–168], or alternatively use cathodic H_2 as electron carriers to drive methane formation [169–172]. Moreover, it has been demonstrated that the integration of MEC with anaerobic digesters (or called "bioelectrochemical reactor, BER") can substantially enhance the production of methane and system stability [173–175], and even remediate AD systems that exhibit process failure [176]. Very recently, several technical attempts have been conducted to couple MEC with AD systems for methane production; indeed, the relatively positive results have been achieved. Sasaki et al. [177]

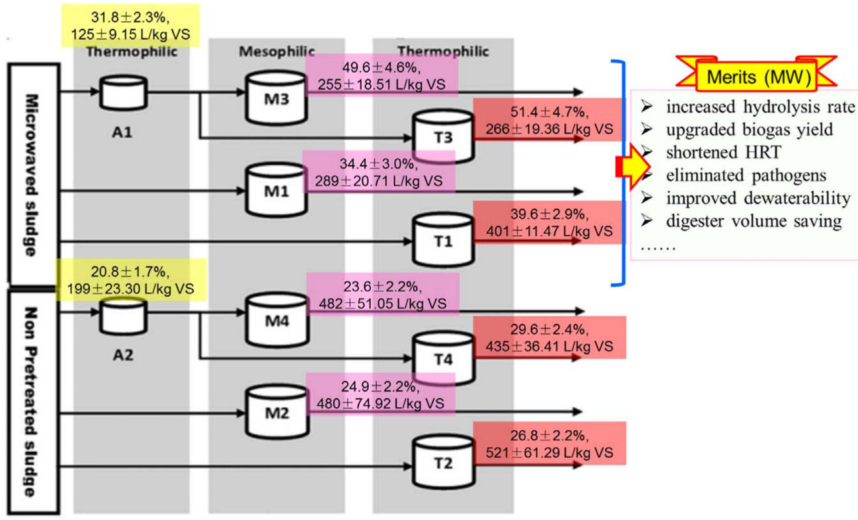

Fig. 6. Schematic diagram of ten digester configurations and the corresponding performances at total SRT 5 d: VS removal (%) and biogas production (L/kg VSremoved) (A: acidogenic thermophilic reactor, M: mesophilic reactor, and T: thermophilic reactor) (further modified from Coelho et al. [52]).

configured a bioelectrochemical reactor (BER) containing carbon fiber fabric (CFF) (BER+CFF) for methane fermentation of thickened sewage sludge. Biogas production in BER+CFF was 3.57 L/L d at HRT of 4 d, increasing by 3.3 times when compared with the control (0.83 L/L d). In a single-chamber MEC fed with sewage sludge, Guo et al. [178] investigated bioelectrochemical enhancement in hydrogen and methane production. 1.7–5.2 and 11.4–13.6-fold increment in hydrogen and methane production were noticed at 1.4 and 1.8 V, respectively. Likewise, Liu et al. [179] reported that with the stimulation of microbial electrolysis (ME), methane production rate was enhanced to 91.8 g CH_4/m^3-reactor d in ME-AD reactor, improving the rate by 3 times compared to the control conditions (30.6 g CH_4/m^3 reactor d in AD). In addition to methane, MEC has been also introduced into bioelectrocatalytic reduction of CO_2 towards the production of other commodities such as formate, acetate [180,181], bioalcohols [182], etc. Regarding the external power supply, besides the commonly used DC power, other alternative power sources such as solar and wind can be also used in this unique anaerobic system, via which both solar/wind and bioenergy is stored simultaneously.

In spite of the promising perspectives outlined above, unlike the other forms of biological processes, there are still many critical challenges associated with MEC-based option that need to be addressed, including slow start-up, pH issues, electrode corrosion/deterioration, high ohmic loss and high overpotentials [174]. Moreover, the performances of this system may differ greatly due to the variations in cells configuration, electrode materials, inoculum sources, substrate compositions and operational conditions. All of these factors have discounted the repeatability and reliability of experimental results, which ultimately restricts the commercial implementation and even up-scaling of this system. Thus, how to virtually use the MEC for real-world application remains a vital challenge. Additionally, though there is a general recognition for electron transfer mechanisms occurring between bacterial cells and electrodes [183–187], a more detailed exploration in microbial community dynamics as well as syntrophic interactions between fermenting bacteria and electroactive bacteria (e.g. exoelectrogens in anode and electrotrophs in cathode) is yet to be performed.

4. Challenges and future perspectives

Anaerobic digestion holds the numerous potential as a substantial approach to harvest bio-methane from sewage sludge. A number of pretreatments as mentioned before have been proposed to enhance this process. At present, mechanical, thermal and chemical pretreatments have been intensively investigated. There are a few patented technologies that have been applied in practical sludge treatment: CambiTHP™, Biothelys® (TH), Biosonator (ultrasonication), Aspal SLUDGE™, Praxair® *Lyso*™ (microwave), BioCrack (electrokinetic disintegration), MicroSludge™, and Cellruptor (HPH) (Table 4). However, the work on biological techniques (TPAD, MEC) are not exhaustive and have still been undergoing lab-scale experiments (Fig. 7a-b). System up-scaling is extremely necessary in order to make the biological processes practically applicable for industrial applications. Besides, to maximize resources recovery from sewage sludge, the digestate has been post-treated to produce value-added byproducts (i.e. struvite ($MgNH_4PO_4{\cdot}6H_2O$) by chemical precipitation [188] (Fig. 7d), or pyrochar and activated carbon via pyrolysis (Fig. 7e) [189]). A recent work also reported the successful struvite crystallization through MEC process, with 20–40% of phosphorus recovery [190]. To our knowledge, up to now no researches have investigated the feasibility of adopting MEC to harvest struvite from the digestate liquor. MEC can also be employed to reduce CO_2 to CH_4 by means of electromethanogenesis [168,169,172], and digestate-derived pyrochar to adsorb the volatile toxic contaminants in biogas, i.e. siloxanes, for biogas purification [2] (Fig. 7c).

Furthermore, pretreatments have the potential to enhance methane productivity, however it does not always strictly speaking. An early work carried out by Climent et al. [90], for instance, has ever claimed that an increment in organic matter solubilization cannot be directly related to an enhancement of the anaerobic digestion of sludge in terms of biogas production. The findings were supported subsequently by Kim et al. [191] with alkali-ultrasonication and Zhen et al. [4] using electrical-alkali process. Likewise, in another separate study, Appels et al. [192] also noticed that soluble organics (SCOD, soluble carbohydrates and soluble proteins) have not influence on the BMP in the observed region. Concomitant liberation of unwanted substances (i.e. biorefractory components [193], excess ammonia [194]) impairs the system stability, inhibiting methane conversion. The opposite observations reflect that for an objective assessment of pretreatment effectiveness, in addition to the commonly used disintegration degree reflected by DD_{COD}, other parameters such as the feature of pretreatment methods provided, the chemical compositions of liberated soluble organics as well as the microbial communities of inoculums added (i.e. methanogenesis activity), have to be considered [4] (Fig. 7a-b).

In addition, a systematic assessment of different pretreatment options is quite necessary for deciding which one would be the most suitable from an industrial point of view. Making a comparison, however, is a very hard task since multiple influencing factors should

Table 4
Summary of the advantages and disadvantages of different pretreatment methods (further modified from [9,12,26,37,200]).

Pretreatment	Mechanisms	Controlling parameters	Advantages	Disadvantages	Commercial technologies
(a) Mechanical					
Ultrasonication	Cavitation (hydro-mechanical shear forces, oxidizing effect)	Power input, exposure time	Increased methane yield, effective in the degradation of cellular wastes, low operational cost, easy maintenance	High energy demand, unsuitable for lignocelluloses, probes require replacement every 1.5–2 years	Biosonator, Sonix, Iwe. Tec, Smart DMS, Sonolyzer, Hiescher
Microwave	Thermal effect (heat intracellular liquor), athermal effect (break up hydrogen bonds, etc.)	Power input, frequency, exposure time	Quick and uniform heating, increased methane yield, pathogen removal, ease of control	High energy demand, scalability, limited to microbial cell-based substrates	Aspal SLUDGE™, Praxair® Lyso™
Electrokinetic disintegration	High-voltage field	Voltage, frequency, exposure time	Increased biogas production, economic benefits	High energy demand, complex equipment, complex operation and maintenance	BioCrack, OpenCEL, PowerMod
HPH	Turbulence, cavitation, shearing forces	Pressure, exposure time, cycle	Easy operation, low cost, increased methane yield, popularity on large scale	High energy demand, complex operation and maintenance	MicroSludge™, Crown, Cellruptor
(b) Thermal	Heating in the range of 100~ °C	Temperature, exposure time, pressure	Increased methane yield, sanitation, odor removal, sludge reduction, improved dewaterability	High energy demand and capital cost, risk of recalcitrant compounds formation, release of ammonia	CambiTHP™, Biothelys®, Exelys, Turbotec, Lysotherm, Biorefinex
(c) Chemical					
Acidic	Hydrolysis of hemicellulose	Dose, exposure time	Increased methane yield, simple device, easy operation, low cost, effective for lignocellulosic biomass	Chemical cost, corrosion, special materials for reactor construction, neutralization before digestion	
Alkali	Solvation, saphonication	Dose, exposure time	Increased methane yield, simple device, easy operation, low cost, suitable for lignin breakdown	Chemical cost, corrosion, special materials for reactor construction, toxicity of Na^+, risk of recalcitrant compounds formation, neutralization before digestion	
Ozonation	Formation of hydroxyl radicals, etc.	Dose, exposure time	Increased methane yield, pathogens removal, sludge reduction, flexible operation	High energy demand, risk of the liberated cellular materials mineralization, increased polymer demand for dewatering	Full-scale operations in excess sludge reduction of WWTP
Fenton	Hydroxyl radicals	Dose, Fe^{2+}/H_2O_2 ratio, exposure time, pH	Increased methane yield, simple device, easy operation, low energy demand	Chemical cost, low pH (~3.0), chemical contamination, risk of scavenging hydroxyl radicals	
Fe(II)-activated persulfate	Sulfate free radicals	Dose, exposure time, pH	Simple device, easy operation, highly improved dewaterability, wide pH range	Chemical cost, chemical contamination, limited data in anaerobic digestion	
(d) Biological					
TPAD	Hydrolysis and acidogenesis in thermophilic stage, acetogenesis and methanogenesis in mesophilic stage	Thermophilic temperature, HRT	Increased methane yield, better solids destruction, use of low-quality thermal energy, low energy demand, sterilization of pathogens	Limited data in parameter optimization, analysis of energy balance and system up-scaling	
MEC	Electromethanogenesis (electrohydrogenesis)	Voltage, pH, temperature	Increased methane yield, purification of biogas, improved process stability	Slow start-up, pH issues, high ohmic loss and overpotentials, highly affected by cells design, electrode materials, etc.	Pilot-scale in wastewater treatment [201,202]

be considered (Table 4). The technical feasibility of one method is dependent upon not only the degree of sludge disintegration and methane conversion efficiency, but energetic and environmental benefits. Besides to increase methane conversion efficiency, pretreatment can also affect the energy required for anaerobic digestion, dewatering, transportation, and ultimate disposal (landfill, incineration, compost, or land application) as well as corresponding GHG emissions [98]. Unfortunately, until yet most of previous studies dealing with sludge pretreatment have mainly focused on the former with hardly considering energetic and environmental issues [12,51,55,59,113]. To simplify the evaluation procedure, researcher often ignore some factors such as dewatering, etc., which are also important costs for the WWTP and could influence the final outcome [7]. The lack of standardization when reporting on the effectiveness of digestion systems remains a huge barrier to meaningful comparison across the literature. The recent works conducted by Pilli and co-workers [51,98,113] proposed an approach to evaluate the effectiveness of pretreatment methods. This calculation involves the energy input for pretreatment, anaerobic digestion, dewatering of the digestate, transporting the dewatered solids from the WWTP to the disposal site and during final disposal (Fig. 7f). They estimated the energy balance of various individual pretreatment processes, e.g. thermal pretreatment (+840 kWh/Mg TDS at 134–140 °C and 3.4 bar for 30 min) [98], Fenton pre-treatment (+285 kWh/Mg TDS at pH 3, 60 g H_2O_2/kg TS and 0.07 g Fe^{2+}/g H_2O_2 for 1 h) [113] and ultrasonication (+7.89 kWh/Mg TDS at 750 W and 20 kHz for 15 min) [51].

The general parametric values considered for the calculations are summarized in Table 5. An example was also given in this study to evaluate the mass-energy balance and GHG emissions in the integrated process of thermal pretreatment (CambiTHP™), mesophilic digestion and land application. In this scenario, assume land application site is 50 km away from the WWTP on the basis of the actual distance between agriculture lands and industries [113,195]. The vehicles used for digested sludge transport are 3 axle semi-trailer with a loading capacity of 14.1 t and fuel efficiency of 35 L of diesel/100 km [195]. The emission coefficients of GHG relative to sludge transport and subsequent land application are estimated according to the actual scenarios from existing facilities [98,195–197]. The corresponding

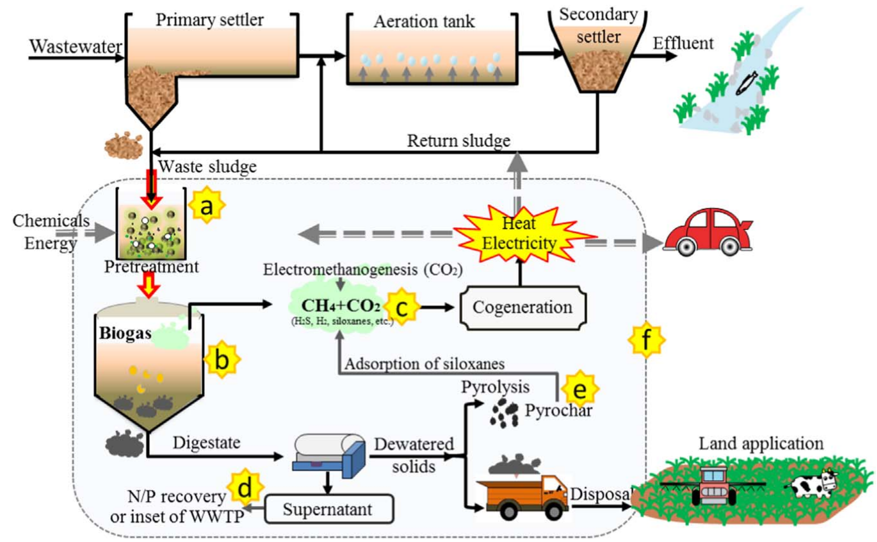

Fig. 7. Process flowchart of the sludge processing steps.

Table 5
General parameters used in mass-energy balance and GHG emissions.

Parameters	Values	References
Volume of sludge to be treated	100,000 m^3/d	
Step (i): pretreatment		
Sludge temperature	12 °C	[195]
Influent DS concentrations	15%	
VS (% of DS)	75%	[203]
Specific gravity	1.023	
Pretreatment conditions	150–165 °C, 20–30 min, 8–9 bar	CambiTHP™
Specific heat of sludge	4200 kJ/m^3 °C	[204]
CO_2 emission due to energy utilization	530 g CO_2/kWh	[98]
Step (ii): anaerobic digestion		
Mesophilic	35 °C	
SRT	20 d	
Energy consumed for mixing	0.005 kW/m^3, 20 min mixing/h	[205]
VS removal $_{control}$	55%	
VS removal $_{pretreated}$	~65%	CambiTHP™
CH_4 yield	0.67 m^3 CH_4/kg VS $_{degraded}$	[203]
Heating value of CH_4	35.8 MJ/m^3 CH_4	[206]
CO_2 emission during CH_4 combustion	1964 g/m^3 CH_4	
Heat loss during operation	150.84 kJ/d m^3	[207]
Step (iii): dewatering		
Energy consumed for dewatering	101.4 kWh/10^3 kg DS	[197]
DS content $_{control}$	20–25%	CambiTHP™
DS content $_{pretreated}$	40%	CambiTHP™
Step (iv): transportation		
Distance (WWTP→land application site)	50 km	[195]
Diesel consumed for transportation	35 L/100 km (3 axle semi-trailer vehicles), 14.1 t of capacity	[195]
CO_2 emission	2730 g CO_2/L-diesel	[195]
CH_4 emission	12 × 10^{-2} g CH_4/L-diesel	[195]
N_2O emission	8 × 10^{-2} g N_2O/L-diesel	[195]
Step (v): land application		
Energy consumed for land application	351.68×10^{-3} kWh/kg DS	[208]
CO_2 emission	17.20 g CO_2/kg DS	[98,196,197]
CH_4 emission	3.18 g CH_4/kg DS	
N_2O emission	30 g CO_2/kg DS	

Note: the heat trapping potential of CH_4 and N_2O are about 21 and 310 times of CO_2 on a per molecule basis, respectively [195].

computation results are demonstrated in Fig. 8. The resultant information would help the industry to determine the performance of one cotreatment route for achieving the optimal sludge conversion and energy recovery as well as the minimum GHG emissions. The emerging approach shows a potential to alleviate such problem (i.e. the lack of standard cost-benefit optimization tool), but further researches are still required to confirm their real potentials. Besides, it is important to admit that for the same pretreatment option, the performance may vary considerably with sludge characteristics, pretreatment conditions, and anaerobic digestion process parameters, increasing the difficulty in comparison. Even worse is that nowadays, the active attempts in the combination of different pretreatment processes, such as alkaline-ultrasound [1], electrical-alkali [4], ultrasound-ozonation [198], microwave-H_2O_2 [199], thermal-NaOH [120], etc., make the comparison more difficult. Other factors that will impact the evaluation results include the operation skill of operator, the maintenance frequency of devices, the local circumstance of labor, land price, the market for renewable energy exchange, etc., in real world scenario. Apparently, for a reliable comparison, supplementary information (e.g. "standard cost-benefit optimization tool") are urgently needed to evaluate such technologies from the energetic, economic and environmental perspectives of view (Fig. 7f).

5. Conclusions

Slow hydrolysis remains a vital constraint on harvest and utilization of chemical energy from sewage sludge. Various disintegration methods have been explored to accelerate the sludge hydrolysis rate and boost the efficiency of anaerobic digestion. Pretreatments can degrade the three-dimensional polymeric backbone (i.e. EPS) and break up rigid cell wall, resulting in the release of intracellular materials whilst enhancing or altering subsequent digester performance. Of the commonly reported approaches, mechanical, thermal and chemical processes have been frequently studied simultaneously with a number of patented technologies being commercially implemented; whereas up to now the research on biological techniques (e.g. TPAD, MEC) is not exhaustive, and more investigations have to been performed to push forward the application of such options from bench experiments to real world sludge treatment. Also there is a potential that the increased solubilization by pretreatment does not conduce to enhanced digestion efficiency, due to the formation and/or introduction of undesired compounds. Further research is needed to clarify clearly the liquor components variations of waste sludge caused by pretreatment (in particular the chemical compositions and biodegradability of each

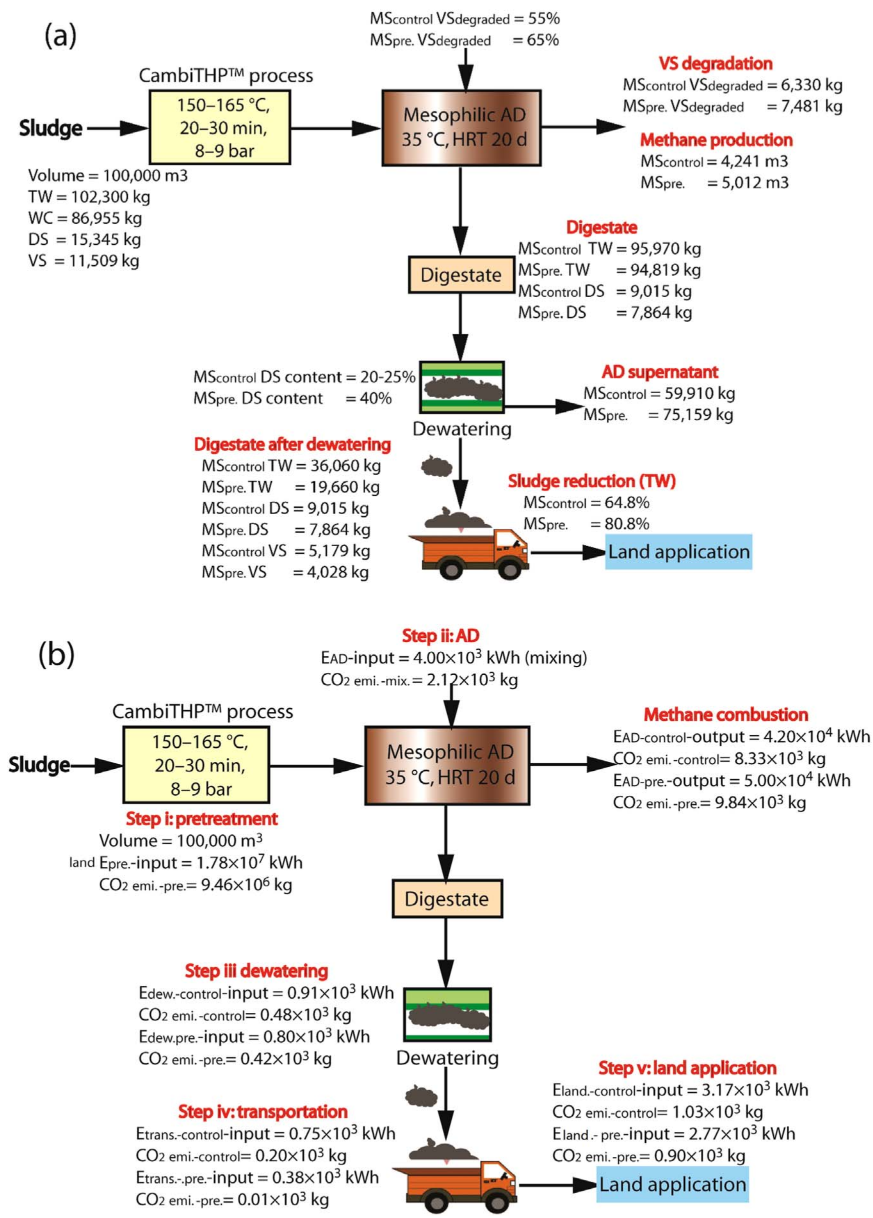

Fig. 8. Mass-energy balance and GHG emissions for the control and thermal pretreated sludge at mesophilic digestion: (a) mass balance and (b) energy balance and GHG emissions (TW: total weight; WC: water content).

portion) as well as the resulting impact on digestion kinetics. More importantly, there is a lack of “standard cost-benefit optimization tool” to assess the technical availability of each pretreatment method from the energetic, economic and environmental perspectives of view, limiting a reliable comparison across the literature. The necessity to establish such standardization should become a vital research issue in the future so as to help the industry to determine the most cost-efficient cotreatment route to ensure the optimal sludge conversion and energy recovery. Besides, several substitutable techniques, such as electro-methanogenesis and pyrochar adsorption to enrich biogas, and microbial electrosynthesis to recover nitrogen and phosphorous from digestate liquor, are also proposed.

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