Review

Disintegration of Wastewater Activated Sludge (WAS) for Improved Biogas Production: A Mini Review

Stanisław Wacławek[1*], Klaudiusz Grübel[2], Daniele Silvestri[1], Vinod V.T. Padil[1], Maria Ząbkowska-Wacławek[3] and Miroslav Černík[1]

1 Centre for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec, Studentská 1402/2, 461 17 Liberec 1, Czech Republic; daniele.silvestri@tul.cz (D.S.); vinod.padil@tul.cz (V.V.T.P); miroslav.cernik@tul.cz (M.Č.)

2 Institute of Environmental Protection and Engineering, University of Bielsko-Biala, Willowa 2, 43-309 Bielsko-Biała, Poland, phone +48 338 279 157; kgrubel@live.ath.edu.pl (K.G.)

3 Faculty of Natural Sciences and Technology, University of Opole, ul. kard. B. Kominka 6, 45-032 Opole, Poland; maria.waclawek@outlook.com (M.Z-W.)

* Correspondence: stanislaw.waclawek@tul.cz; Tel.: +420 485 353 006

Abstract: Due to rapid urbanization, the quantity of wastewater treatment plants (WWTP) has increased, and with it the amount of waste generated by them. Sustainable management of this waste can lead to the creation of energy-rich biogas through the fermentation process. This review presents recent advances in the anaerobic digestion process resulting in greater biogas production. Disintegration techniques for enhancing waste activated sludge fermentation can be generally partitioned into biological, physical and chemical, each of which are covered in this review. These disintegration techniques were compared mainly in terms of their biogas yield. It was found that ultrasonic and microwave disintegration provides the highest biogas yield (>500%); however, they are also the most energy demanding (>10,000 kJ kg^{-1} total solids).

Keywords: biogas; renewable energy; anaerobic digestion; waste activated sludge; disintegration

---

1. Introduction

The continuous increase in the use of fossil fuel in modern society and the harmful effects of greenhouse gases on the environment will see research of alternative energy sources becoming more important and even mandatory in the future. In this context, research focussing on the improvement of biogas production has become essential. Moreover, due to the increase in urbanization, the number of wastewater treatment plants (WWTP) has increased, and since the wastes (e.g. waste activated sludge (WAS)) generated from the WWTP are considered dangerous for the environment, it is important to develop efficient processes for their treatment [1].

Raw activated sludge is hydrated to a level of 97%-99% and the rest contains solid and dissolved matter, minerals and organic substances, coagulants, gels and trapped gas bubbles. However, the stabilized sediment is most often hydrated to a level of 60%-88% [1–3].

The basic process of sludge utilisation consists in spreading it over the surface of the soil in order to fertilize it or improve its properties. Sludge utilisation is used in the following areas:

- in agriculture, for growing crops,
- for the reclamation of land, including land for agricultural purposes,
- for the adaptation of land to specific needs resulting from waste management plans, spatial development plans or decisions on building and land development conditions,
- for the production of compost,
- for the cultivation of *flora* not intended for consumption [2].

Unless it contains excessive amounts of heavy metals, stabilized sludge can improve the agrotechnical state of fertilized soils, because it contains a high concentration of available organic phosphorus, lime and magnesium compounds.

Each producer of waste, including WAS, is obligated to handle it in a manner consistent with the principles of waste management and the requirements of environmental protection and waste management plans [4]. Firstly, waste should be subject to a recovery process and if it is impossible for technological reasons or is not justified for ecological or economic reasons, it should be subjected to disposal [2]. The composition of WAS is extremely varied and depends on many factors, for example, the WWTP and the method of treatment applied [5]. There are many issues concerning WAS including, dissolved heavy metals and/or toxic organic substances [6]: dioxins and furans, PCBs, and pesticides. At present, there are 500 substances classified in 15 different categories. With the exception of heavy metals, European Union regulations still lack strict limits on these substances in WAS.

Anaerobic digestion (AD) is one of the most commonly applied processes for WAS treatment as it is considered to be sustainable. It is also capable of decreasing the weight of the sludge, and stabilising and decreasing its toxicity. Another advantage of this method is that it produces biofuel (biogas), making it not only an environmentally feasible option but also cost-beneficial. With this in mind, it is not surprising that the number of WWTPs producing and storing biogas is increasing each year. For example, in 2009 there were 6,227 of these plants in Europe, by 2015 there were 17,376, an almost three -fold increase in only six years [7]. In China alone there are currently more than one million of these plants [8].

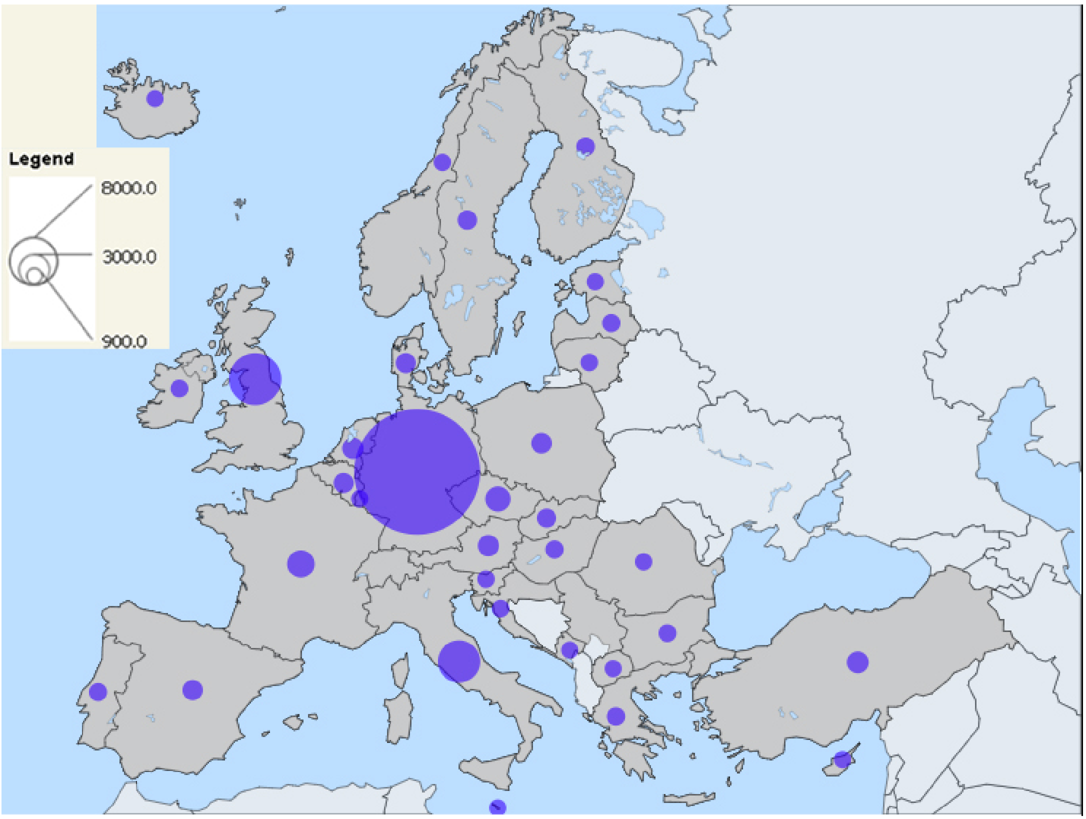

Figure 1. Primary production of biogas in the EU (tonnes of oil equivalent · 1000; source: https://ec.europa.eu/eurostat; 2018).

Biogas can be made from a range of organic substances and can be used to produce heat, power, heat and power (combined) or as a fuel for vehicles. Biogas contains methane, carbon dioxide, and nitrogen in different proportions and in trace concentrations also hydrogen sulphide, hydrogen, ammonia, oxygen, and carbon monoxide [9], siloxanes and aromatic and halogenated compounds (also depending on the fermentation/pre-treatment type) [10]. Primary production of biogas in the

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1
Peer-reviewed version available at Energies 2019, 12, 21; doi:10.3390/en12010021

European Union is shown in Fig. 1 and the typical characteristic of biogas can be found in Table 1 [11].

Table 1. Typical characteristic of biogas.

Constituents	Energy (kW m^{-3})	Fuel equivalent (L oil m^{-3} biogas)	Ignition temperature (°C)	Critical pressure (bar)	Critical temperature (°C)	Normal density (kg m^{-3})
CH_4: 55-70%, CO_2: 30-45%, other gases	6.0-6.5	0.6-0.65	650-750	75-89	-82.5	1.2

Anaerobic digestion consists of four steps i.e. hydrolysis, acidogenesis, acetogenesis and methanogenesis [12]. It is a complex process achievable only under strict anaerobic conditions, with hydrolysis considered as a rate limiting step [13]. During hydrolysis, lipids, proteins, polysaccharides and soluble organic matter are all degraded, with the final products being further treated through acidogenesis to yield volatile fatty acids (acidogenesis = generation of acids also known as VFAs) and other by-products [14]. The acidogenesis step is followed by acetogenesis, during which the VFAs are digested by acetogenic microorganisms producing an even simpler molecule, acetate. The last step is methanogenesis, during which methane is generated. Methanogenesis involves two methanogenic microorganisms, one group uses acetate to obtain methane and CO_2 and the other uses hydrogen to produce methane [15]. This whole process, including the contribution of organic substances (chemical oxygen demand (COD)) and bacteria involved in it, is illustrated in Fig. 2.

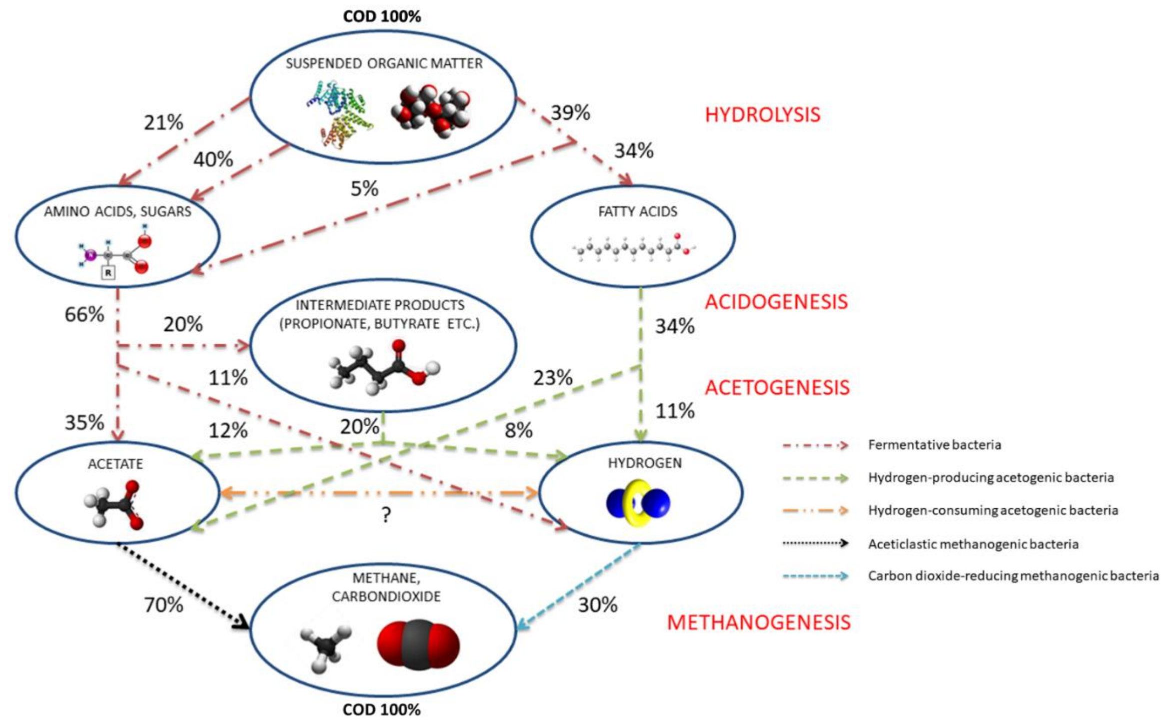

Figure 2. Proposed diagram of methane production during anaerobic digestion (based on [16]).

Biogas is a renewable fuel, which is considered to be more eco-friendly than conventional energy reserves; therefore, rapid development in this field is based on improving the biogas yield and especially by improving the pre-treatment process of WAS.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at Energies 2019, 12, 21; doi:10.3390/en12010021

Pre-treatment of WAS is one of the most crucial steps before AD as it eliminates the disadvantages of the rate-limiting step – hydrolysis, and can often significantly enhance the yield of biogas with a simultaneous reduction of the sludge cake. In addition, several of these methods can efficiently reduce the toxicity of WAS by degrading toxic and persistent microorganisms and molecules.

For various reasons, it is hard to compare the effectiveness of different pre-treatment methods used in wastewater technologies. The most important variables that make unambiguous comparison impossible are the type of sludge (*inter alia*: waste activated, primary, digested, sludge age) and the anaerobic conditions used (*inter alia*: temperature, continuous/batch, hydraulic retention time (HRT)).

However, this mini-review paper focuses only on the recent advances in WAS pre-treatment methods, which positively impacts subsequent biogas production.

2. Pre-treatment methods

Pre-treatment methods can be described as being either separate or hybrid processes (not discussed in this mini-review). These processes are applied to provide the optimum results for a range of purposes. Before selecting the technology, the pre-treatment goals must be clearly defined, because improvement of one of the processes can negatively affect another treatment stage.

As mentioned above, selection of the disintegration method depends heavily on the type of sludge. Müller [17] suggests that the most effectively method for primary sludges and sludges with high lignocellulose content is enzymatic pre-treatment. However, it could be less suitable for WAS or secondary sludges as they degrade themselves before enzymatic hydrolysis starts.

The vast majority of studies devoted to disintegration methods focus on the implementation of these methods for activated sludge or secondary sludge. This is due to the fact that primary sludges are most frequently composed of easily-degraded components (no treatment needed) or secondary sludges, and are mainly formed by microorganisms whose cell walls prevent rapid degradation.

One of the major components of WAS flocs are extracellular polymeric substances (EPS) comprised mainly of a proteins (e.g. enzymes), carbohydrates, humic matter and, to a smaller amount, uronic and deoxyribonucleic (DNA) acids and lipids. EPS, multivalent cations, hydrophobic interactions and hydrogen bonds while interacting together cause formation of a network of polymeric substances in the waste activated sludge [18,19]. All of this leads to long retention times required for biological stabilisation. Recently, many pre-treatment methods focus on EPS degradation and there are also many methods for their extraction [20,21].

Several different pre-treatment/disintegration methods are used specifically to improve anaerobic digestion e.g. biological, chemical and physical methods as well as their combinations. Essentially, sludge pre-treatment is used to break down the cell walls of microbes generally to reduce the molecular weight of substances in WAS, releasing the intracellular matter, which becomes more accessible to anaerobic microbes and consequently enhancement of the anaerobic digestion.

The most important objectives of disintegration/pre-treatment methods include:

- Simple access to the organic substances that were trapped inside the biomass and their release into the supernatant/liquid phase, as well as to intracellular enzymes that cause direct decomposition of pollutants,
- Release of organic substrate (in the case of disintegration of surplus activated sludge; often represented as chemical oxygen demand (COD)) that can be an easily digestible organic carbon source for the denitrification process, in the case of its absence in incoming sewage to the bioreactor. The increase in COD solubilization can be often correlated with the increase in methane production [22],
- Removing activated sludge foam generated on the surface of bioreactors as well as elimination of foaming in digestion chambers and secondary settling tanks,
- **Increase in the biogas production and biogas yield and hence energy production with faster digestion.**

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at Energies 2019, 12, 21; doi:10.3390/en12010021

In recent years, several pre-treatment / disintegration methods have been applied both on a bench and technical scale, for example by using thermal energy [23,24], enzymes [25], ozonisation [26], acidification [27], alkalization [28,29], high pressure [30,31], mechanical grinding [32] and ultrasound energy [33,34]. In general, these techniques can be split into 3 categories: biological, physical and chemical (Fig. 3).

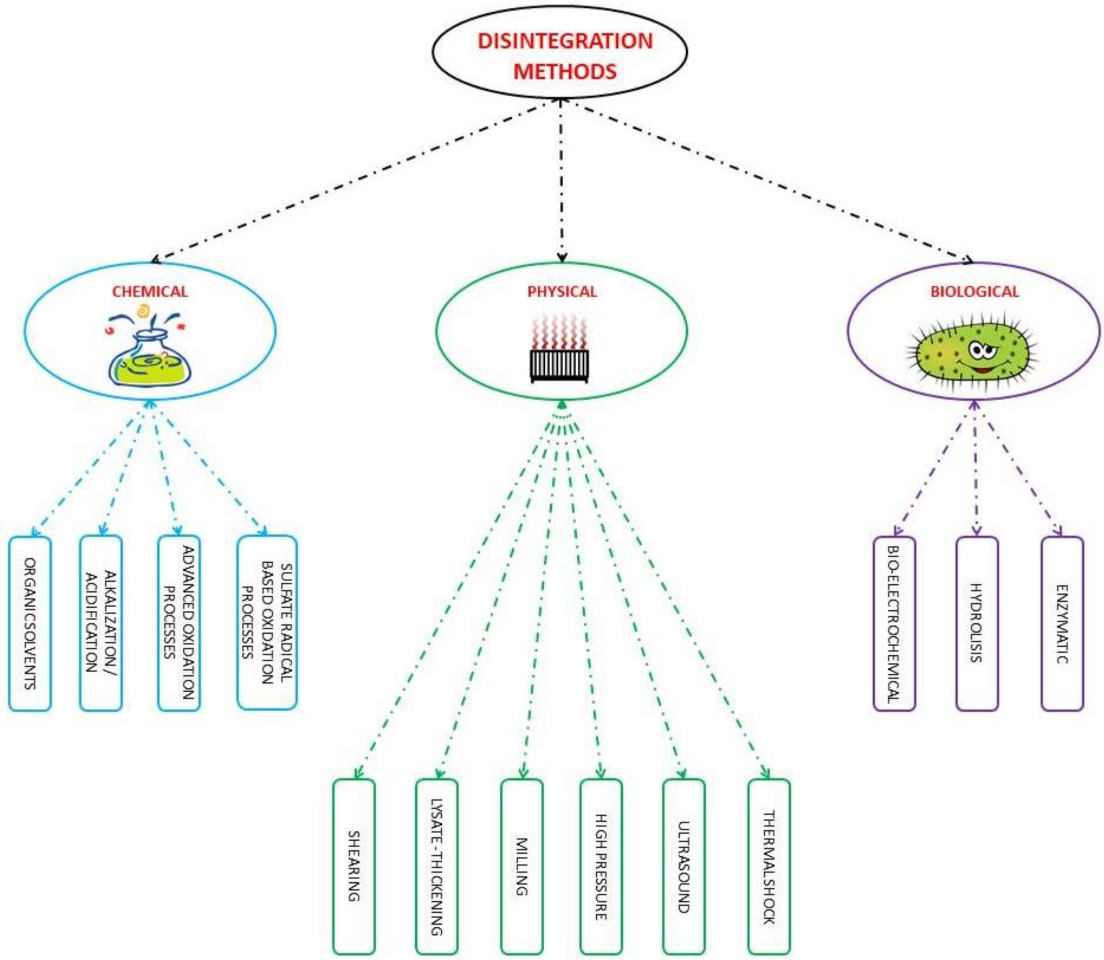

Figure 3. Diagram showing the available disintegration methods for waste activated sludge.

2.1. Biological

Biological pre-treatment (Tab. 2) can utilise anaerobic or aerobic processes [35,36]. Anaerobic pre-treatment is one of the most commonly used in sludge pre-treatment [37], this process can effectively destroy pathogens, reduce volatile solids and enhance biogas production [38–42].

Ai et al. [43] concluded in their recent research that adding *Bacillus coagulants* can promote the hydrolysis and acidogenesis process with no negative effect on the methanogenesis process. In order to obtain the sludge disintegration, it is possible to use enzymes, which are biologically derived molecules that work as a catalyst (also known as a biocatalyst). It is possible to classify these enzymes into six basic classes: oxidoreductases, ligases, transferases, lyases, hydrolysases, and isomerases. Enzymatic lysis by the enzyme catalysing the reaction leads to the breaking down of bonds and compounds constituting the cell wall of the microorganisms. The enzymes can help decompose the organic matter, i.e. turn it into smaller molecules [25,36,37,44–57]. Very recently, Prajapati et al. [58] successfully used a bio-electrochemical process to enhance the methane production from sewage sludge with food waste.

2.2. Chemical

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at Energies 2019, 12, 21; doi:10.3390/en12010021

Chemical pre-treatment is another efficient and cost-effective process for hydrolysing the membranes and the cell walls and hence increase the solubility of the organic matter that is located inside the cells. The most commonly used and popular chemical pre-treatment methods before anaerobic digestion are alkalization [59] or acidification [46,60,61].

The most commonly used alkali compound reagents are NaOH [62], $Ca(OH)_2$ [63] and KOH [63]. Alkali pre-treatment can solubilize the cell membranes, releasing the intracellular matter from the cells in solution, which becomes available for the fermentation process. The intracellular matter essentially formed by lipid proteins and hydrocarbons is decomposed in the soluble substances that are available for the microorganisms [64]. The advantages of alkali methods are their high efficiency and the easiness of performing the process [65].

On the other hand, oxidation techniques are often used because of their enormous efficiency. Traditional oxidation techniques include Fenton reactions, and photocatalytic and ozonation processes. All of the above-mentioned techniques have one thing in common, namely the formation of a hydroxyl radical. These processes are also known as advanced oxidation processes (AOP). Ozonation pre-treatment includes two different types of oxidation processes i.e. ozonolysis and hydroxyl radical reactions, which depend mainly on the pH values. It was reported that at low pH the ozone reacts selectively with the organic molecules constituted by C=C, -OH, CH_3, $-OCH_3$ and others [66], and at pH >8 the ozone generates $^{\cdot}O_2^{-}$ and $HO_2^{\cdot}$ radicals [67], more details can be found in [66,68–81]. On the other hand, Fenton reactions involve the reaction of hydrogen peroxide with divalent iron producing hydroxyl radicals, and has been used in environmental matrices (including WAS) for a long period of time [82,83]. Although, these methods have been tested for many years for WAS pre-treatment, there are still some innovative solutions being reported. For example, in a recent study Hallaji et al. [84] reported the possibility to increase the methane production by 72% with a combined FNA (free nitrous acid)/Fenton reaction pre-treatment process. The possibility to increase methane production by ~200% with a combination of micro aerobic hydrolysis and the addition of trace metals has also been reported [85]. Anjum et al. [86] recently reported the possibility to enhance the biogas production using photocatalytic disintegration of WAS, whereby this procedure increased the biogas production by 1.6 times.

It should be noted that whereas the hydroxyl radical pre-treatment of WAS have been known for some time, sulphate radical pre-treatment (activated peroxydisulfate or peroxymonosulphate (persulphates)) has only been known for the last few years; however, several limitations disable their *in situ* application for now. Peroxydisulphate (PDS) is a strong oxidant used with success for the disintegration of WAS by several authors [20,87–90]. In order to form sulphate and hydroxyl radicals, persulphates need to be activated, usually by heat [91], metal [92], UV [93] and alkaline conditions [94] among others [95].

Many oxidation techniques, including Fenton reactions [96]) and new reactions concerning peroxomonosulphate (PMS; [97]) and dimethyldioxirane (DMDO), can cause the alteration of refractory organic matter into easily accessible and soluble biochemical oxygen demand (BOD), and subsequently improve the biogas yield [83] (Tab. 2).

Recently, a newly used oxidant for this purpose, peracetic acid (PAA), was proposed to improve anaerobic digestion [98].

2.2. Physical methods

Physical and mechanical treatments of WAS work in basically the same way, the cell walls are broken and flocs break up by the application of force/external energy. Disintegration of the WAS with the use of mechanical forces causes the fragmentation of flocks and effective lysis of bacterial cells, leading to the release of organic substances and therefore an increase in biogas production.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at Energies 2019, 12, 21; doi:10.3390/en12010021

The effect of mechanical disintegration of WAS on the efficiency of AD has been investigated for a long period. Mechanical shearing, lysate-thickening centrifuge [99], milling technology [100], and high pressure technology [49,101–106] are some of the main techniques.

Hydrodynamic cavitation triggered by the Venturi effect is a promising process for pretreatment of waste activated sludge prior to mesophilic fermentation according to many authors, including Machnicka et al. [107]. Furthermore, mesophilic digestion trials have reported a significant increase in the biogas production of approximately 36.1% and 62.1 6% for 10% and 30% of the volume of foam added to the digestion chamber, respectively.

Ultrasonic methods have also been included as physical treatment in this review; however, they can also be included as AOPs. These methods involve two different processes: cavitation, which is promoted at low frequencies, and the formation of radicals ($^{\cdot}OH$, $HO_2^{\cdot}$, $H^{\cdot}$) due to the chemical reactions at high frequencies [36]. To induce cavitation, the process has to run at a certain frequency (<100 kHz), the ultrasound creates gas bubbles that when collapsing produce hydromechanical forces, which disintegrate the macromolecules [31,108,109]. The extreme conditions that occur during the cavitation process can cause generation of hydroxyl radicals, which can degrade volatile and non-volatile pollutants. Ultrasonication can enhance the WAS digestibility by damaging the physical, chemical and biological properties of the sludge. Ultrasonic lysis accelerates the hydrolysis reactions by disrupting the cells. Within the explosion (cavitational) of transient bubbles, a certain amount of soluble particulate organic matter can be made completely soluble. Ultrasound is considered to be one of the most efficient sludge pre-treatments for sludge floc disintegration [72,108,110–115]. For example, Lizama et al.[116] reported an increase in biogas production after ultrasonic treatment of 560% (Tab. 2).

Compared to mechanical techniques, thermal disintegration processes consumes more energy, but they can be used e.g. by using heat exchangers or by the use of steam to the WAS. Thermal pre-treatment processes can take place at a wide range of temperatures from 60 to 270 °C. The processes at a temperature of <100 °C are considered as low temperature processes and those taking place at a temperature of >100 °C are high temperature processes [48,49,72,117–120].

The optimal temperature treatment is frequently stated to be around 170 °C [121]. Ennouri et al. [122] reported that at a thermal pre-treatment temperature of 120 °C the biogas yield increased by 37%.

However, Dwyer et al. [123] reported that COD solubilisation increased at temperatures above 150 °C but there was no increase in the methane production. According to Batstone et al. [124], the main disadvantages of thermal pre-treatment are linked to the costs and increased ammonia inhibition.

Another pre-treatment process that has already shown to improve anaerobic digestion is microwave pre-treatment [125]. Microwave pre-treatment is reported to be a good substitute for thermal pre-treatment, increasing the concentration of soluble proteins in solution [126] and improving biogas [127,128] production and disinfection [129]. Microwave irradiation has two main effects, thermal and non-thermal. The thermal effect is due to the electric field that interacts with proteins, fats and H_2O. The non-thermal effect results in the break down of hydrogen bonds and the consequent death of microorganisms [130].

Other recent methods involve the application of low temperatures for WAS treatment known as freezing/thawing [23,24,131].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at *Energies* **2019**, *12*, 21; doi:10.3390/en12010021

Table 2. Recent advances in the pretreatment of WAS for biogas production enhancement.

Disintegration type	Treatment type/condition	Anaerobic digestion condition	Results	Reference
Biological	Amylase + protease	37 °C	+23% biogas yield	[25]
	Lysozyme	37 °C	+45% COD removal	[132]
	Biological hydrolysis	42 °C	+744 mg · L^{-1} acetic acid	[133]
	Micro-aerobic hydrolysis	25 °C	+186% methane yield	[85]
Chemical	1.11 mg HNO_2-N L^{-1}	37 °C	+ 32% methane yield	[134]
	FNA (Free Nitrous Acid): 2.5 mg L^{-1} H_2O_2: 5 mg L^{-1}	-	+72% methane yield	[84]
	20 mg NaOH g^{-1}TS	37 °C	+35% methane yield	[135]
	157 g NaOH kg^{-1}TS	37 °C	+34% methane yield	[136]
	0.1 g $K_2S_2O_8$ g^{-1}SS	35 °C	180% methane yield	[88]
	Nano-layered TiO_2	40 °C	+8% COD	[137]
	ZnO-ZnS@polyaniline	35 °C	1.6 times higher biogas yield	[86]
Physical and hybrid	70 °C 50 °C	-	+148% methane yield	[138]
	70 °C 90 °C	55 °C	+160% methane yield	[139]
	100 °C	33 °C	+251% biogas yield	[140]
	134 °C	55 °C	+38.5% biogas yield	[141]
	170 °C	35 °C	+60% methane yield	[142]
	25 W/L	35 °C	+95% methane yield	[143]
	0.2 W/g	37 °C	+27% biogas yield	[144]
	14,000 kJ/kg TS	35 °C	+570% biogas yield	[145]

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 19 November 2018 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at Energies 2019, 12, 21; doi:10.3390/en12010021

	10,000 kJ kg^{-1} + 90 °C	37 °C	+30% biochemical methane potential	[146]
	pH 12 24 kJ g^{-1} TS	-	+22% dissolved organic matters	[147]
	135.4 mg of free ammonia L^{-1} with 70 °C	35 °C	+52% faster hydrolysis	[148]
	Ultrasounds: 125 W	35 °C	+68% methane yield in biogas	[149]
	25,000 kJ kg^{-1} TS	36 °C	+560% biogas yield	[116]

3. Conclusions

In this review we have evaluated various disintegration methods of waste activated sludge for enhanced production of eco-fuel – biogas. The pre-treatments are focused mainly on enhancing the disintegration method and improving the hydrolysis and gaining more biogas in the AD process. We have presented three types of pre-treatment processes (biological, chemical and physical), their various strengths, weaknesses and recent advances. Some pre-treatment processes are more efficient in reducing the biomass [72], and others work better for the solubilization of organic matter [150] or for the cell disintegration. In addition, the different pre-treatment processes generate differing costs depending on e.g. the volume of WAS used, have differing reaction times and effects on biogas generation. Biological pre-treatment is usually slower than other types of treatment and can last several days. Chemical and physical methods are faster and easier to implement; however, they are often more energy demanding. A very good example of this can be taken from [116,145] where the application of microwaves or ultrasonic energy increased biogas production by >500%; however, these processes are very energy-demanding.

Funding: The research presented in this article was supported by the Ministry of Education, Youth and Sports in the framework of the targeted support of the "National Programme for Sustainability I" LO 1201 and the OPR & DI project "Extension of CxI facilities" (CZ.1.05/2.1.00/19.0386). The authors also acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project no. LM2015073. This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic and the European Union – European Structural and Investment Funds in the frames of Operational Program Research, Development and Education – project Hybrid Materials for Hierarchical Structures (HyHi, Reg. No. CZ.02.1.01/0.0/0.0/16_019/0000843).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mudhoo, A. *Biogas Production Pretreatment Methods in Anaerobic Digestion*; John Wiley & Sons, 2012; ISBN 1118404076.

2. Chernicharo, C. A. de L. *Anaerobic reactors*; ISBN 1843391643.

3. Begum, L. *Advanced processes and technologies for enhanced anaerobic digestion*; Green Nook Press, 2014; ISBN 0993904505.

4. United States Environmental Protection Agency *National Hazardous Waste Management Plan 2008-2012*; 2008; ISBN 9781840952988.

5. Fytili, D.; Zabaniotou, A. Utilization of sewage sludge in EU application of old and new methods—A review. *Renew. Sustain. Energy Rev.* **2008**, *12*, 116–140, doi:10.1016/J.RSER.2006.05.014.

6. Wzorek, M. Characterisation of the properties of alternative fuels containing sewage sludge. *Fuel Process. Technol.* **2012**, *104*, 80–89, doi:10.1016/J.FUPROC.2012.04.023.

7. Mathiasson, A. *Future of Biogas Europe*; 2017;

8. Banu, J. R.; Kavitha, S. Various Sludge Pretreatments: Their Impact on Biogas Generation. In *Waste Biomass Management – A Holistic Approach*; Springer International Publishing: Cham, 2017; pp. 39–71.

9. Ullah Khan, I.; Hafiz Dzarfan Othman, M.; Hashim, H.; Matsuura, T.; Ismail, A. F.; Rezaei-DashtArzhandi, M.; Wan Azelee, I. Biogas as a renewable energy fuel – A review of biogas upgrading, utilisation and storage. *Energy Convers. Manag.* **2017**, *150*, 277–294, doi:10.1016/J.ENCONMAN.2017.08.035.

10. Rasi, S.; Veijanen, A.; Rintala, J. Trace compounds of biogas from different biogas production plants. *Energy* **2007**, *32*, 1375–1380, doi:10.1016/J.ENERGY.2006.10.018.

11. Deublein, D.; Steinhauser, A. *Biogas from Waste and Renewable Resources : an Introduction.*; Wiley-VCH, 2008; ISBN 9783527621705.

12. Meyer, T.; Edwards, E. A. Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water Res.* **2014**, *65*, 321–349, doi:10.1016/J.WATRES.2014.07.022.

13. Aquino, S. F.; Stuckey, D. C. Integrated model of the production of soluble microbial products (SMP) and extracellular polymeric substances (EPS) in anaerobic chemostats during transient conditions. *Biochem. Eng. J.* **2008**, *38*, 138–146, doi:10.1016/J.BEJ.2007.06.010.

14. Pham, H. D.; Seon, J.; Lee, S. C.; Song, M.; Woo, H.-C. Maximization of volatile fatty acids production from alginate in acidogenesis. *Bioresour. Technol.* **2013**, *148*, 601–604, doi:10.1016/J.BIORTECH.2013.08.128.

15. Mao, C.; Feng, Y.; Wang, X.; Ren, G. Review on research achievements of biogas from anaerobic digestion. *Renew. Sustain. Energy Rev.* 2015, *45*, 540–555.

16. Gujer, W.; Zehnder, A. J. B. Conversion processes in anaerobic digestion. *Water Sci. Technol.* **1983**, *15*, 127–167, doi:10.2166/wst.1983.0164.

17. Müller, J. A. Prospects and problems of sludge pre-treatment processes. In *Water Science and Technology*; 2001.

18. Wawrzynczyk, J. Enzymatic treatment of wastewater sludge. Sludge solubilisation, improvement of anaerobic digestion and extraction of extracellular polymeric substances Available online:

http://www.dissertations.se/dissertation/e13b392027/.

19. Beijer, R. Enzymatic treatement of wastewater sludge in presence of a cation binding agent : improved solubilisation and increased methane production. **2008**.

20. Shi, Y.; Yang, J.; Yu, W.; Zhang, S.; Liang, S.; Song, J.; Xu, Q.; Ye, N.; He, S.; Yang, C.; Hu, J. Synergetic conditioning of sewage sludge via Fe2+/persulfate and skeleton builder: Effect on sludge characteristics and dewaterability. *Chem. Eng. J.* **2015**, *270*, 572–581, doi:10.1016/j.cej.2015.01.122.

21. Li, X. Y.; Yang, S. F. Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge. *Water Res.* **2007**, *41*, 1022–1030, doi:10.1016/j.watres.2006.06.037.

22. Carrère, H.; Bougrier, C.; Castets, D.; Delgenès, J. P. Impact of initial biodegradability on sludge anaerobic digestion enhancement by thermal pretreatment. *J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng.* **2008**, *43*, 1551–1555, doi:10.1080/10934520802293735.

23. Hu, K.; Jiang, J.-Q.; Zhao, Q.-L.; Lee, D.-J.; Wang, K.; Qiu, W. Conditioning of wastewater sludge using freezing and thawing: Role of curing. *Water Res.* **2011**, *45*, 5969–5976, doi:10.1016/j.watres.2011.08.064.

24. Nowicka, E.; Machnicka, A.; Grübel, K. Improving of anaerobic digestion by dry ice disintegration of activated sludge. *Ecol. Chem. Eng. A* **2014**, *Vol. 21*, doi:10.2428/ECEA.2014.21(2)17.

25. Yu, S.; Zhang, G.; Li, J.; Zhao, Z.; Kang, X. Effect of endogenous hydrolytic enzymes pretreatment on the anaerobic digestion of sludge. *Bioresour. Technol.* **2013**, *146*, 758–761, doi:10.1016/j.biortech.2013.07.087.

26. Glaze, W. H.; Kang, J.-W.; Chapin, D. H. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone Sci. Eng.* **1987**, *9*, 335–352, doi:10.1080/01919518708552148.

27. Woodard, S. E.; Wukasch, R. F. A HYDROLYSIS/THICKENING/FILTRATION PROCESS FOR THE TREATMENT OF WASTE ACTIVATED SLUDGE. *Water Sci. Technol.* **1994**, *30*, 29–38, doi:10.2166/wst.1994.0056.

28. Grübel, K.; Suschka, J. Hybrid alkali-hydrodynamic disintegration of waste-activated sludge before two-stage anaerobic digestion process. *Environ. Sci. Pollut. Res. 22*, 7258–7270, doi:10.1007/s11356-014-3705-y.

29. Grubel, K.; Machnicka, A.; Waclawek, S.; Grűbel, K.; Machnicka, A.; Wacławek, S. Impact of alkalization of surplus activated sludge on biogas production. *Ecol. Chem. Eng. S* **2013**, *20*, 343–351, doi:10.2478/eces-2013-0025.

30. Gogate, P. R.; Shirgaonkar, I. Z.; Sivakumar, M.; Senthilkumar, P.; Vichare, N. P.; Pandit, A. B. Cavitation reactors: Efficiency assessment using a model reaction. *AIChE J.* **2001**, *47*, 2526–2538, doi:10.1002/aic.690471115.

31. Machnicka, A.; Grubel, K.; Suschka, J. The use of hydrodynamic disintegration as a means to improve anaerobic digestion of activated sludge. *Water SA* **2009**, *35*, 129–132, doi:10.4314/wsa.v35i1.CITATIONS.

32. Müller, J. Disintegration as a key-step in sewage sludge treatment. *Water Sci. Technol.* **2000**, *41*, 123–130, doi:10.2166/wst.2000.0151.

33. Antoniadis, A.; Poulios, I.; Nikolakaki, E.; Mantzavinos, D. Sonochemical disinfection of municipal wastewater. *J. Hazard. Mater.* **2007**, *146*, 492–495, doi:10.1016/J.JHAZMAT.2007.04.065.

34. Zhang, P.; Zhang, G.; Wang, W. Ultrasonic treatment of biological sludge: Floc disintegration, cell lysis and inactivation. *Bioresour. Technol.* **2007**, *98*, 207–210, doi:10.1016/J.BIORTECH.2005.12.002.

35. Ali, M.; Zhang, J.; Raga, R.; Lavagnolo, M. C.; Pivato, A.; Wang, X.; Zhang, Y.; Cossu, R.; Yue, D. Effectiveness of aerobic pretreatment of municipal solid waste for accelerating biogas generation during simulated landfilling. *Front. Environ. Sci. Eng.* **2018**, *12*, 5, doi:10.1007/s11783-018-1031-1.

36. Carrère, H.; Dumas, C.; Battimelli, A.; Batstone, D. J.; Delgenès, J. P.; Steyer, J. P.; Ferrer, I. Pretreatment methods to improve sludge anaerobic degradability: A review. *J. Hazard. Mater.* **2010**, *183*, 1–15.

37. Merrylin, J.; Kumar, S. A.; Kaliappan, S.; Yeom, I.-T.; Banu, J. R. Biological pretreatment of non-flocculated sludge augments the biogas production in the anaerobic digestion of the pretreated waste activated sludge. *Environ. Technol.* **2013**, *34*, 2113–2123, doi:10.1080/09593330.2013.810294.

38. Gebreeyessus, G. D.; Jenicek, P. Thermophilic versus Mesophilic Anaerobic Digestion of Sewage Sludge: A Comparative Review. *Bioeng. (Basel, Switzerland)* **2016**, *3*, doi:10.3390/bioengineering3020015.

39. Ferrer, I.; Vázquez, F.; Font, X. Long term operation of a thermophilic anaerobic reactor: Process stability and efficiency at decreasing sludge retention time. *Bioresour. Technol.* **2010**, *101*, 2972–2980, doi:10.1016/j.biortech.2009.12.006.

40. Ponsá, S.; Ferrer, I.; Vázquez, F.; Font, X. Optimization of the hydrolytic–acidogenic anaerobic digestion stage (55°C) of sewage sludge: Influence of pH and solid content. *Water Res.* **2008**, *42*, 3972–3980, doi:10.1016/j.watres.2008.07.002.

41. Ge, H.; Jensen, P. D.; Batstone, D. J. Temperature phased anaerobic digestion increases apparent hydrolysis rate for waste activated sludge. *Water Res.* **2011**, *45*, 1597–1606, doi:10.1016/J.WATRES.2010.11.042.

42. Jang, H. M.; Park, S. K.; Ha, J. H.; Park, J. M. Microbial community structure in a thermophilic aerobic digester used as a sludge pretreatment process for the mesophilic anaerobic digestion and the enhancement of methane production. *Bioresour. Technol.* **2013**, *145*, 80–89, doi:10.1016/j.biortech.2013.01.094.

43. Ai, S.; Liu, H.; Wu, M.; Zeng, G.; Yang, C. Roles of acid-producing bacteria in anaerobic digestion of waste activated sludge. *Front. Environ. Sci. Eng.* **2018**, *12*, doi:10.1007/s11783-018-1050-y.

44. Recktenwald, M.; Wawrzynczyk, J.; Dey, E. S.; Norrlöw, O. Enhanced efficiency of industrial-scale anaerobic digestion by the addition of glycosidic enzymes. *J. Environ. Sci. Heal. Part A* **2008**, *43*, 1536–1540, doi:10.1080/10934520802293693.

45. Jang, H. M.; Cho, H. U.; Park, S. K.; Ha, J. H.; Park, J. M. Influence of thermophilic aerobic digestion as a sludge pre-treatment and solids retention time of mesophilic anaerobic digestion on the methane production, sludge digestion and microbial communities in a sequential digestion process. *Water Res.* **2014**, *48*, 1–14, doi:10.1016/J.WATRES.2013.06.041.

46. Bayr, S.; Kaparaju, P.; Rintala, J. Screening pretreatment methods to enhance thermophilic anaerobic digestion of pulp and paper mill wastewater treatment secondary sludge. *Chem. Eng. J.* **2013**, *223*, 479–486, doi:10.1016/J.CEJ.2013.02.119.

47. Kavitha, S.; Jayashree, C.; Adish Kumar, S.; Yeom, I. T.; Rajesh Banu, J. The enhancement of anaerobic biodegradability of waste activated sludge by surfactant mediated biological pretreatment. *Bioresour. Technol.* **2014**, *168*, 159–166, doi:10.1016/J.BIORTECH.2014.01.118.

48. Climent, M.; Ferrer, I.; Baeza, M. del M.; Artola, A.; Vázquez, F.; Font, X. Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions. *Chem. Eng. J.* **2007**, *133*, 335–342, doi:10.1016/J.CEJ.2007.02.020.

49. Barjenbruch, M.; Kopplow, O. Enzymatic, mechanical and thermal pre-treatment of surplus sludge. *Adv. Environ. Res.* **2003**, *7*, 715–720, doi:10.1016/S1093-0191(02)00032-1.

50. Hasegawa, S.; Shiota, N.; Katsura, K.; Akashi, A. Solubilization of organic sludge by thermophilic aerobic bacteria as a pretreatment for anaerobic digestion. *Water Sci. Technol.* **2000**, *41*, 163–9.

51. You, M. Y.; Chai, T. Y.; Pan, Y.; Zhu, Y. N.; Cao, Y. H.; Li, X. J.; Xie, Y. H.; Han, J.; Zhu, T. Review of Excess Sludge Disintegration Research. *Adv. Mater. Res.* **2013**, *726–731*, 2949–2955, doi:10.4028/www.scientific.net/AMR.726-731.2949.

52. Gopi Kumar, S.; Merrylin, J.; Kaliappan, S.; Adish Kumar, S.; Tae Yeom, I.; Rajesh Banu, J. Effect of cation binding agents on sludge solubilization potential of bacteria. *Biotechnol. Bioprocess Eng.* **2012**, *17*, 346–352, doi:10.1007/s12257-011-0465-0.

53. Mayhew, M. E.; Le, M. S.; Ratcliff, R. A novel approach to pathogen reduction in biosolids: the enzymic hydrolyser. *Water Sci. Technol.* **2002**, *46*, 427–34.

54. Mayhew, M.; Le, M. S.; Brade, C. E.; Harrison, D. THE UNITED UTITLITIES 'ENZYMIC HYDROLYSIS PROCESS' – VALIDATION OF PHASED DIGESTION AT FULL SCALE TO ENHANCE PATHOGEN REMOVAL. *Proc. Water Environ. Fed.* **2003**, *2003*, 1000–1013, doi:10.2175/193864703784292197.

55. MIAH, M. S.; TADA, C.; SAWAYAMA, S. Enhancement of Biogas Production from Sewage Sludge with the Addition of Geobacillus sp. Strain AT1 Culture. *Japanese J. Water Treat. Biol.* **2004**, *40*, 97–104, doi:10.2521/jswtb.40.97.

56. Wawrzynczyk, J.; Dey, E.; Norrlöw, O.; la Cour Jansen, J. Alternative Method for Sludge Reduction Using Commercial Enzymes. In; 2003.

57. Davidsson, Å.; Wawrzynczyk, J.; Norrlöw, O.; la Cour Jansen, J. Strategies for enzyme dosing to enhance anaerobic digestion of sewage sludge. *J. Residuals Sci. Technol. 4(1), pp 1-7* **2007**, *4*, 1–7.

Peer-reviewed version available at *Energies* **2019**, *12*, 21; doi:10.3390/en12010021

58. Prajapati, K. B.; Singh, R. Kinetic modelling of methane production during bio-electrolysis from anaerobic co-digestion of sewage sludge and food waste. *Bioresour. Technol.* **2018**, *263*, 491–498, doi:10.1016/j.biortech.2018.05.036.

59. Kim, J.; Park, C.; Kim, T.; Lee, M.; Kim, S.; Eung-wook Kim, S.; Lee, J. Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge. *J. Biosci. Bioeng.* **2003**, *95*, 271–275, doi:10.1016/S1389-1723(03)80028-2.

60. Parthiba Karthikeyan, O.; Trably, E.; Mehariya, S.; Bernet, N.; Wong, J. W. C.; Carrere, H. Pretreatment of food waste for methane and hydrogen recovery: A review. *Bioresour. Technol.* **2018**, *249*, 1025–1039, doi:10.1016/J.BIORTECH.2017.09.105.

61. Wang, Q.; Jiang, G.; Ye, L.; Yuan, Z. Enhancing methane production from waste activated sludge using combined free nitrous acid and heat pre-treatment. *Water Res.* **2014**, *63*, 71–80, doi:10.1016/J.WATRES.2014.06.010.

62. Silvestri, D.; Wacławek, S.; Gončuková, Z.; Padil, V. V. T.; Grübel, K.; Černík, M. A new method for assessment of the sludge disintegration degree with the use of differential centrifugal sedimentation. *Environ. Technol.* **2018**, 1–8, doi:10.1080/09593330.2018.1477839.

63. Lee, I.; Han, J.-I. The effects of waste-activated sludge pretreatment using hydrodynamic cavitation for methane production. *Ultrason. Sonochem.* **2013**, *20*, 1450–1455, doi:10.1016/J.ULTSONCH.2013.03.006.

64. Modenbach, A. A.; Nokes, S. E. The use of high-solids loadings in biomass pretreatment-a review. *Biotechnol. Bioeng.* **2012**, *109*, 1430–1442, doi:10.1002/bit.24464.

65. Wonglertarak, W.; Wichitsathian, B. Alkaline Pretreatment of Waste Activated Sludge in Anaerobic Digestion. *J. Clean Energy Technol.* **2014**, 118–121, doi:10.7763/JOCET.2014.V2.104.

66. Ikehata, K.; Gamal El-Din, M. The Journal of the International Ozone Association Degradation of Recalcitrant Surfactants in Wastewater by Ozonation and Advanced Oxidation Processes: A Review. **2010**, doi:10.1080/01919510490482160.

67. Wang, F.; Smith, D. W.; El-Din, M. G. Application of advanced oxidation methods for landfill leachate treatment – A review. *J. Environ. Eng. Sci.* **2003**, *2*, 413–427, doi:10.1139/s03-058.

68. Sievers, M.; Ried, A.; Koll, R. Sludge treatment by ozonation Ð evaluation of full-scale results. *Water Sci. Technol.* **2004**, *49*, 247–253, doi:10.2166/wst.2004.0275.

69. Ak, M. S.; Muz, M.; Komesli, O. T.; Gökçay, C. F. Enhancement of bio-gas production and xenobiotics degradation during anaerobic sludge digestion by ozone treated feed sludge. *Chem. Eng. J.* **2013**, *230*, 499–505, doi:10.1016/J.CEJ.2013.06.113.

70. Silvestre, G.; Ruiz, B.; Fiter, M.; Ferrer, C.; Berlanga, J. G.; Alonso, S.; Canut, A. Ozonation as a Pre-treatment for Anaerobic Digestion of Waste-Activated Sludge: Effect of the Ozone Doses. *Ozone Sci. Eng.* **2015**, *37*, 316–322, doi:10.1080/01919512.2014.985817.

71. Carballa, M.; Manterola, G.; Larrea, L.; Ternes, T.; Omil, F.; Lema, J. M. Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products. *Chemosphere* **2007**, *67*, 1444–1452, doi:10.1016/j.chemosphere.2006.10.004.

72. Bougrier, C.; Delgenès, J.-P.; Carrère, H. Combination of Thermal Treatments and Anaerobic Digestion to Reduce Sewage Sludge Quantity and Improve Biogas Yield. *Process Saf. Environ. Prot.* **2006**, *84*, 280–284, doi:10.1205/PSEP.05162.

73. Battimelli, A.; Millet, C.; Delgenès, J. P.; Moletta, R. Anaerobic digestion of waste activated sludge combined with ozone post-treatment and recycling. *Water Sci. Technol.* **2003**, *48*, 61–8.

74. Carbajo, J. B.; Petre, A. L.; Rosal, R.; Berná, A.; Letón, P.; García-Calvo, E.; Perdigón-Melón, J. A. Ozonation as pre-treatment of activated sludge process of a wastewater containing benzalkonium chloride and NiO nanoparticles. *Chem. Eng. J.* **2016**, *283*, 740–749, doi:10.1016/J.CEJ.2015.08.001.

75. Oller, I.; Malato, S.; Sánchez-Pérez, J. A. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. *Sci. Total Environ.* 2011, *409*, 4141–4166.

76. Chu, C. .; Lee, D. .; Chang, B.-V.; You, C. .; Tay, J. . "Weak" ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids. *Water Res.* **2002**, *36*, 2681–2688, doi:10.1016/S0043-1354(01)00515-2.

77. Paul, E.; Camacho, P.; Sperandio, M.; Ginestet, P. Technical and Economical Evaluation of a Thermal, and Two Oxidative Techniques for the Reduction of Excess Sludge Production. *Process Saf. Environ. Prot.* **2006**, *84*, 247–252, doi:10.1205/PSEP.05207.

78. Saktaywin, W.; Tsuno, H.; Nagare, H.; Soyama, T.; Weerapakkaroon, J. Advanced sewage treatment process with excess sludge reduction and phosphorus recovery. *Water Res.* **2005**, *39*, 902–910, doi:10.1016/J.WATRES.2004.11.035.

79. Yeom, I. T.; Lee, K. R.; Ahn, K. H.; Lee, S. H. Effects of ozone treatment on the biodegradability of sludge from municipal wastewater treatment plants. *Water Sci. Technol.* **2002**, *46*, 421–5.

80. Bougrier, C.; Battimelli, A.; Delgenes, J.-P.; Carrere, H. Combined Ozone Pretreatment and Anaerobic Digestion for the Reduction of Biological Sludge Production in Wastewater Treatment. *Ozone Sci. Eng.* **2007**, *29*, 201–206, doi:10.1080/01919510701296754.

81. Valo, A.; Carrère, H.; Delgenès, J. P. Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion. *J. Chem. Technol. Biotechnol.* **2004**, *79*, 1197–1203, doi:10.1002/jctb.1106.

82. Barbusinski, K. Fenton reaction - Controversy concerning the chemistry. *Ecol. Chem. Eng. S/Chemia i in·zynieria Ekol. S* **2009**, *16*, 347–358.

83. Dewil, R.; Appels, L.; Baeyens, J.; Degrève, J. Peroxidation enhances the biogas production in the anaerobic digestion of biosolids. *J. Hazard. Mater.* **2007**, *146*, 577–581, doi:10.1016/J.JHAZMAT.2007.04.059.

Peer-reviewed version available at *Energies* **2019**, *12*, 21; doi:10.3390/en12010021

84. Hallaji, S. M.; Torabian, A.; Aminzadeh, B.; Zahedi, S.; Eshtiaghi, N. Improvement of anaerobic digestion of sewage mixed sludge using free nitrous acid and Fenton pre-treatment. *Biotechnol. Biofuels* **2018**, *11*, 233, doi:10.1186/s13068-018-1235-4.

85. Montalvo, S.; Vielma, S.; Borja, R.; Huiliñir, C.; Guerrero, L. Increase in biogas production in anaerobic sludge digestion by combining aerobic hydrolysis and addition of metallic wastes. *Renew. Energy* **2018**, *123*, 541–548, doi:10.1016/J.RENENE.2018.02.004.

86. Anjum, M.; Al-Talhi, H. A.; Mohamed, S. A.; Kumar, R.; Barakat, M. A. Visible light photocatalytic disintegration of waste activated sludge for enhancing biogas production. *J. Environ. Manage.* **2018**, *216*, 120–127, doi:10.1016/J.JENVMAN.2017.07.064.

87. Wacławek, S.; Grübel, K.; Chłąd, Z.; Dudziak, M.; Chład, Z.; Dudziak, M.; Chłąd, Z.; Dudziak, M. Impact of peroxydisulphate on disintegration and sedimentation properties of municipal wastewater activated sludge. *Chem. Pap.* **2015**, *69*, 1473–1480, doi:10.1515/chempap-2015-0169.

88. Sun, D.; Liang, H.; Ma, C. Enhancement of sewage sludge anaerobic digestibility by sulfate radical pretreatment. *Adv. Mater. Res. (Durnten-Zurich, Switz.)* **2012**, *518–523*, 3358–3362, doi:10.4028/www.scientific.net/AMR.518-523.3358.

89. Liu, C.; Wu, B.; Chen, X. Sulfate radical-based oxidation for sludge treatment: A review. *Chem. Eng. J.* 2018, *335*, 865–875.

90. Wang, S.; Wang, J. Activation of peroxymonosulfate by sludge-derived biochar for the degradation of triclosan in water and wastewater. *Chem. Eng. J.* **2018**, *356*, 350–358, doi:10.1016/J.CEJ.2018.09.062.

91. Ji, Y.; Xie, W.; Fan, Y.; Shi, Y.; Kong, D.; Lu, J. Degradation of trimethoprim by thermo-activated persulfate oxidation: Reaction kinetics and transformation mechanisms. *Chem. Eng. J.* **2016**, *286*, 16–24, doi:10.1016/j.cej.2015.10.050.

92. Kim, C.; Ahn, J. Y.; Kim, T. Y.; Shin, W. S.; Hwang, I. Activation of Persulfate by Nanosized Zero-Valent Iron (NZVI): Mechanisms and Transformation Products of NZVI. *Environ. Sci. Technol.* **2018**, *52*, 3625–3633, doi:10.1021/acs.est.7b05847.

93. Zhang, R.; Sun, P.; Boyer, T. H.; Zhao, L.; Huang, C.-H. Degradation of Pharmaceuticals and Metabolite in Synthetic Human Urine by UV, UV/H_2O_2, and UV/PDS. *Environ. Sci. Technol.* **2015**, *49*, 3056–3066, doi:10.1021/es504799n.

94. Siegrist, R. L.; Crimi, M.; Brown, R. *In Situ Chemical Oxidation: Technology Description and Status*; 2011; ISBN 978-1-4419-7825-7.

95. Wacławek, S.; Lutze, H. V.; Grübel, K.; Padil, V. V. T.; Černík, M.; Dionysiou, D. D. Chemistry of persulfates in water and wastewater treatment: A review. *Chem. Eng. J.* **2017**, *330*, 44–62, doi:10.1016/j.cej.2017.07.132.

96. Neyens, E.; Baeyens, J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater.* **2003**, *98*, 33–50.

97. Jin, B.; Niu, J.; Dai, J.; Li, N.; Zhou, P.; Niu, J.; Zhang, J.; Tao, H.; Ma, Z.; Zhang, Z. New insights into the enhancement of biochemical degradation potential from waste activated sludge with low organic content by Potassium Monopersulfate treatment. *Bioresour. Technol.* **2018**, *265*, 8–16, doi:10.1016/J.BIORTECH.2018.05.032.

98. Shang, M.; Hou, H. Studies on Effect of Peracetic Acid Pretreatment on Anaerobic Fermentation Biogas Production from Sludge. In *2009 Asia-Pacific Power and Energy Engineering Conference*; IEEE, 2009; pp. 1–3.

99. Zábranská, J.; Dohányos, M.; Jenícek, P.; Kutil, J. Disintegration of excess activated sludge--evaluation and experience of full-scale applications. *Water Sci. Technol.* **2006**, *53*, 229–36.

100. Elliott, A.; Mahmood, T. Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues. *Water Res.* **2007**, *41*, 4273–4286, doi:10.1016/J.WATRES.2007.06.017.

101. Engelhart, M.; Krueger, M.; Kopp, J.; Dichtl, N. Effects of disintegration on anaerobic degradation of sewage excess sludge in downflow stationary fixed film digesters. *Water Sci. Technol.* **2000**, *41 3*, 171–179.

102. Kumar, P. S.; Pandit, A. B. Modeling Hydrodynamic Cavitation. *Chem. Eng. Technol.* **1999**, *22*, 1017–1027, doi:10.1002/(SICI)1521-4125(199912)22:12<1017::AID-CEAT1017>3.0.CO;2-L.

103. Grűbel, K.; Machnicka, A. Use of Hydrodynamic Disintegration to Accelerate Anaerobic Digestion of Surplus Activated Sludge. *Water Environ. Res.* **2009**, *81*, 2420–2426.

104. Mirota, K.; Grubel, K.; Machnicka, A. Design and assessment of cavitational device for enhancement of sewage sludge fermentation | Badania i ocena możliwości stosowania zwężki kawitacyjnej do intensyfikacji procesu fermentacji osadów ściekowych. *Ochr. Sr.* **2011**, *33*, 47–52.

105. Senthil Kumar, P.; Siva Kumar, M.; Pandit, A. . Experimental quantification of chemical effects of hydrodynamic cavitation. *Chem. Eng. Sci.* **2000**, *55*, 1633–1639, doi:10.1016/S0009-2509(99)00435-2.

106. Vichare, N. P.; Gogate, P. R.; Pandit, A. B. Optimization of Hydrodynamic Cavitation Using a Model Reaction. *Chem. Eng. Technol.* **2000**, *23*, 683–690, doi:10.1002/1521-4125(200008)23:8<683::AID-CEAT683>3.0.CO;2-9.

107. Machnicka, A.; Grübel, K.; Mirota, K. Considerations of impact of Venturi effect on mesophilic digestion. *Ecol. Chem. Eng. S* **2015**, *22*, 645–658, doi:10.1515/eces-2015-0039.

108. Tiehm, A.; Nickel, K.; Zellhorn, M.; Neis, U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Res.* **2001**, *35*, 2003–2009, doi:10.1016/S0043-1354(00)00468-1.

109. Machnicka, A.; Grübel, K.; Suschka, J. The use of disintegrated foam to accelerate anaerobic digestion of activated sludge. *Arch. Environ. Prot.* **2009**, *35*, 11–19, doi:10.4314/wsa.v35i1.CITATIONS.

110. Zhou, Z.; Yang, Y.; Li, X. Effects of ultrasound pretreatment on the characteristic evolutions of drinking water treatment sludge and its impact on coagulation property of sludge recycling process. *Ultrason. Sonochem.* **2015**, *27*, 62–71, doi:10.1016/j.ultsonch.2015.04.018.

 doi:10.20944/preprints201811.0441.v1

Peer-reviewed version available at *Energies* **2019**, *12*, 21; doi:10.3390/en12010021

111. Aylin Alagöz, B.; Yenigün, O.; Erdinçler, A. Ultrasound assisted biogas production from co-digestion of wastewater sludges and agricultural wastes: Comparison with microwave pre-treatment. *Ultrason. Sonochem.* **2018**, *40*, 193–200, doi:10.1016/J.ULTSONCH.2017.05.014.

112. Bougrier, C.; Carrère, H.; Delgenès, J. P. Solubilisation of waste-activated sludge by ultrasonic treatment. *Chem. Eng. J.* **2005**, *106*, 163–169.

113. Salsabil, M. R.; Prorot, A.; Casellas, M.; Dagot, C. Pre-treatment of activated sludge: Effect of sonication on aerobic and anaerobic digestibility. *Chem. Eng. J.* **2009**, *148*, 327–335, doi:10.1016/J.CEJ.2008.09.003.

114. Mao, T.; Show, K.-Y. Influence of ultrasonication on anaerobic bioconversion of sludge. *Water Environ. Res.* **2007**, *79*, 436–41.

115. Mao, T.; Show, K. Y. Performance of high-rate sludge digesters fed with sonicated sludge. *Water Sci. Technol.* **2006**, *54*, 27–33.

116. Lizama, A. C.; Figueiras, C. C.; Pedreguera, A. Z.; Ruiz Espinoza, J. E. Effect of ultrasonic pretreatment on the semicontinuous anaerobic digestion of waste activated sludge with increasing loading rates. *Int. Biodeterior. Biodegradation* **2018**, *130*, 32–39, doi:10.1016/J.IBIOD.2018.03.013.

117. Ferrer, I.; Ponsá, S.; Vázquez, F.; Font, X. Increasing biogas production by thermal (70 °C) sludge pre-treatment prior to thermophilic anaerobic digestion. *Biochem. Eng. J.* **2008**, *42*, 186–192, doi:10.1016/J.BEJ.2008.06.020.

118. Ferrer, I.; Serrano, E.; Ponsa, S.; Vazquez, F.; Font, X. Enhancement of thermophilic anaerobic sludge digestion by 70 ºC pre-treatment: Energy considerations. *J. Residuals Sci. Technol.* **2009**, *6*, 8.

119. Hendriks, A. T. W. M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* **2009**, *100*, 10–18, doi:10.1016/J.BIORTECH.2008.05.027.

120. Delgenès, J. P.; Penaud, V.; Torrijos, M.; Moletta, R. Investigations on the changes in anaerobic biodegradability and biotoxicity of an industrial microbial biomass induced by a thermochemical pretreatment. *Water Sci. Technol.* **2000**, *41*, 137–44.

121. Kepp, U.; Machenbach, I.; Weisz, N.; Solheim, O. E. Enhanced stabilisation of sewage sludge through thermal hydrolysis - three years of experience with full scale plant. *Water Sci. Technol.* **2000**, *42*, 89–96, doi:10.2166/wst.2000.0178.

122. Ennouri, H.; Miladi, B.; Diaz, S. Z.; Güelfo, L. A. F.; Solera, R.; Hamdi, M.; Bouallagui, H. Effect of thermal pretreatment on the biogas production and microbial communities balance during anaerobic digestion of urban and industrial waste activated sludge. *Bioresour. Technol.* **2016**, *214*, 184–191, doi:10.1016/J.BIORTECH.2016.04.076.

123. Dwyer, J.; Starrenburg, D.; Tait, S.; Barr, K.; Batstone, D. J.; Lant, P. Decreasing activated sludge thermal hydrolysis temperature reduces product colour, without decreasing degradability. *Water Res.* **2008**, *42*, 4699–4709, doi:10.1016/J.WATRES.2008.08.019.

Peer-reviewed version available at *Energies* **2019**, *12*, 21; doi:10.3390/en12010021

124. Batstone, D. J.; Balthes, C.; Barr, K. Model assisted startup of anaerobic digesters fed with thermally hydrolysed activated sludge. *Water Sci. Technol.* **2010**, *62*, 1661–1666, doi:10.2166/wst.2010.487.

125. Bohdziewicz, J.; Kuglarz, M.; Grubel, K. Influence of microwave pre-treatment on the digestion and higienisation of waste activated sludge. *Ecol. Chem. Eng. S* **2014**, *21*, 447–464, doi:10.2478/eces-2014-0033.

126. Yi, W. G.; Lo, K. V.; Mavinic, D. S. Effects of microwave, ultrasonic and enzymatic treatment on chemical and physical properties of waste-activated sludge. *J. Environ. Sci. Heal. Part A* **2014**, *49*, 203–209, doi:10.1080/10934529.2013.838880.

127. Park, W.-J.; Ahn, J.-H. Effects of Microwave Pretreatment on Mesophilic Anaerobic Digestion for Mixture of Primary and Secondary Sludges Compared with Thermal Pretreatment. *Environ. Eng. Res.* **2011**, *16*, 103–109, doi:10.4491/eer.2011.16.2.103.

128. Kuglarz, M.; Karakashev, D.; Angelidaki, I. Microwave and thermal pretreatment as methods for increasing the biogas potential of secondary sludge from municipal wastewater treatment plants. *Bioresour. Technol.* **2013**, *134*, 290–297, doi:10.1016/J.BIORTECH.2013.02.001.

129. Eskicioglu, C.; Kennedy, K. J.; Droste, R. L. Enhanced disinfection and methane production from sewage sludge by microwave irradiation. *Desalination* **2009**, *248*, 279–285, doi:10.1016/j.desal.2008.05.066.

130. Tang, B.; Yu, L.; Huang, S.; Luo, J.; Zhuo, Y. Energy efficiency of pre-treating excess sewage sludge with microwave irradiation. *Bioresour. Technol.* **2010**, *101*, 5092–5097, doi:10.1016/J.BIORTECH.2010.01.132.

131. Montusiewicz, A.; Lebiocka, M.; Rożej, A.; Zacharska, E.; Pawłowski, L. Freezing/thawing effects on anaerobic digestion of mixed sewage sludge. *Bioresour. Technol.* **2010**, *101*, 3466–3473, doi:10.1016/J.BIORTECH.2009.12.125.

132. Lakshmi, M. V.; Merrylin, J.; Kavitha, S.; Kumar, S. A.; Banu, J. R.; Yeom, I.-T. Solubilization of municipal sewage waste activated sludge by novel lytic bacterial strains. *Environ. Sci. Pollut. Res.* **2014**, *21*, 2733–2743, doi:10.1007/s11356-013-2228-2.

133. Ding, H. H.; Chang, S.; Liu, Y. Biological hydrolysis pretreatment on secondary sludge: Enhancement of anaerobic digestion and mechanism study. *Bioresour. Technol.* **2017**, *244*, 989–995, doi:10.1016/J.BIORTECH.2017.08.064.

134. Wang, Q.; Jiang, G.; Ye, L.; Yuan, Z. Accepted Manuscript Enhancing methane production from waste activated sludge using combined free nitrous acid and heat pre-treatment. *Water Res.* **2014**, doi:10.1016/j.watres.2014.06.010.

135. Zhang, S.; Guo, H.; Du, L.; Liang, J.; Lu, X.; Li, N.; Zhang, K. Influence of NaOH and thermal pretreatment on dewatered activated sludge solubilisation and subsequent anaerobic digestion: Focused on high-solid state. *Bioresour. Technol.* **2015**, *185*, 171–177, doi:10.1016/j.biortech.2015.02.050.

136. Ruiz-Hernando, M.; Martín-Díaz, J.; Labanda, J.; Mata-Alvarez, J.; Llorens, J.; Lucena, F.; Astals, S. Effect of ultrasound, low-temperature thermal and alkali pre-treatments on waste activated sludge rheology, hygienization and methane potential. *Water Res.* **2014**, *61*, 119–129, doi:10.1016/J.WATRES.2014.05.012.

137. Godvin Sharmila, V.; Rajesh Banu, J.; Gunasekaran, M.; Angappane, S.; Yeom, I. T. Nano-layered TiO_2 for effective bacterial disintegration of waste activated sludge and biogas production. *J. Chem. Technol. Biotechnol.* **2018**, *93*, 2701–2709, doi:10.1002/jctb.5626.

138. Alqaralleh, R. M.; Kennedy, K.; Delatolla, R. Improving biogas production from anaerobic co-digestion of Thickened Waste Activated Sludge (TWAS) and fat, oil and grease (FOG) using a dual-stage hyper-thermophilic/thermophilic semi-continuous reactor. *J. Environ. Manage.* **2018**, *217*, 416–428, doi:10.1016/J.JENVMAN.2018.03.123.

139. Mirmasoumi, S.; Khoshbakhti Saray, R.; Ebrahimi, S. Evaluation of thermal pretreatment and digestion temperature rise in a biogas fueled combined cooling, heat, and power system using exergo-economic analysis. *Energy Convers. Manag.* **2018**, *163*, 219–238, doi:10.1016/J.ENCONMAN.2018.02.069.

140. Kang, X.; Liu, Y.; Li, X.; Yuan, Y.; Du, M. Two-stage mesophilic anaerobic digestion from waste activated sludge enhanced by low-temperature thermal hydrolysis. *Desalin. Water Treat.* **2016**, *57*, 7607–7614, doi:10.1080/19443994.2015.1025440.

141. Gagliano, M. C.; Braguglia, C. M.; Gianico, A.; Mininni, G.; Nakamura, K.; Rossetti, S. Thermophilic anaerobic digestion of thermal pretreated sludge: Role of microbial community structure and correlation with process performances. *Water Res.* **2015**, *68*, 498–509, doi:10.1016/j.watres.2014.10.031.

142. Abelleira-Pereira, J. M.; Pérez-Elvira, S. I.; Sánchez-Oneto, J.; de la Cruz, R.; Portela, J. R.; Nebot, E. Enhancement of methane production in mesophilic anaerobic digestion of secondary sewage sludge by advanced thermal hydrolysis pretreatment. *Water Res.* **2015**, *71*, 330–340, doi:10.1016/J.WATRES.2014.12.027.

143. Martín, M. Á.; González, I.; Serrano, A.; Siles, J. Á. Evaluation of the improvement of sonication pre-treatment in the anaerobic digestion of sewage sludge. *J. Environ. Manage.* **2015**, *147*, 330–337, doi:10.1016/j.jenvman.2014.09.022.

144. Houtmeyers, S.; Degrève, J.; Willems, K.; Dewil, R.; Appels, L. Comparing the influence of low power ultrasonic and microwave pre-treatments on the solubilisation and semi-continuous anaerobic digestion of waste activated sludge. *Bioresour. Technol.* **2014**, *171*, 44–49, doi:10.1016/J.BIORTECH.2014.08.029.

145. Ebenezer, A. V.; Arulazhagan, P.; Adish Kumar, S.; Yeom, I.-T.; Rajesh Banu, J. Effect of deflocculation on the efficiency of low-energy microwave pretreatment and anaerobic biodegradation of waste activated sludge. *Appl. Energy* **2015**, *145*, 104–110, doi:10.1016/J.APENERGY.2015.01.133.

146. Zhen, G.; Lu, X.; Kato, H.; Zhao, Y.; Li, Y.-Y. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. *Renew. Sustain. Energy Rev.* **2017**, *69*, 559–577, doi:10.1016/j.rser.2016.11.187.

147. Lu, D.; Xiao, K.; Chen, Y.; Soh, Y. N. A.; Zhou, Y. Transformation of dissolved organic matters produced from alkaline-ultrasonic sludge pretreatment in anaerobic digestion: From macro to micro. *Water Res.* **2018**, *142*, 138–146, doi:10.1016/J.WATRES.2018.05.044.

148. Liu, X.; Xu, Q.; Wang, D.; Zhao, J.; Wu, Y.; Liu, Y.; Ni, B.-J.; Wang, Q.; Zeng, G.; Li, X.; Yang, Q. Improved

methane production from waste activated sludge by combining free ammonia with heat pretreatment: Performance, mechanisms and applications. *Bioresour. Technol.* **2018**, *268*, 230–236, doi:10.1016/J.BIORTECH.2018.07.109.

149. Zieliński, M.; Dębowski, M.; Krzemieniewski, M.; Rusanowska, P.; Zielińska, M.; Cydzik-Kwiatkowska, A.; Głowacka-Gil, A. Application of an Innovative Ultrasound Disintegrator for Sewage Sludge Conditioning Before Methane Fermentation. *J. Ecol. Eng.* **2018**, *19*, 240–247, doi:10.12911/22998993/89817.

150. Aboulfotoh, A. M.; Gohary, E. H. El; Monayeri, O. D. El Effect Of Thermal Pretreatment On The Solubilization Of Organic Matters In A Mixture Of Primary And Waste Activated Sludge. *J. Urban Environ. Eng.* **2015**, *9*, 82–88, doi:10.4090/juee.2013.v9n1.82-88.