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Review Article
Pretreatment Methods of Organic Wastes for Biogas Production

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Abstract
During biogas production, the rate-determining step for the conversion of complex organic matter is the hydrolysis. Different pretreatment methods aid in facilitating the anaerobic digestion by increasing the rate of organic matter hydrolysis. This in effect results in enhanced production of biogas and aids in waste stabilization as well as disposal. This review gives an overview of the methods used in pretreating organic wastes including mechanical, thermal, chemical and biological. In addition, hybrid method (physico-chemical) involving more than one technology has been useful in enhancing waste solubilization and anaerobic digestion. Thus, economic analysis including the cost of operation and the benefits derived in form of biogas, waste minimization and treatment should be considered during the selection of any pretreatment methods for large scale application.

Key words: Pretreatment, organic waste, biogas, anaerobic digestion, waste solubilization, volatile solids

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INTRODUCTION

Biogas is made up of 50-70% CH_4, 30-50% CO_2 and some notable impurities such as NH_3, H_2S, siloxane and halides (Bakhov *et al*., 2014; Yentekakis *et al*., 2008). The concentration of each of these compounds depends on the composition of the raw materials and the process conditions used during the digestion (Bond and Templeton, 2011). The calorific value of biogas is dependent on the methane content where 1 m^3 of raw biogas contains 60% CH_4 with calorific value of 21.5 MJ equivalents to 5.97 kW h of electricity under standard temperature and pressure. Thus, biogas as a renewable energy source burns with smoke-less flame has been effectively used in developing countries for cooking, lighting and heating. Besides these, it can be upgraded to be used in internal combustion engines, power generation facilities and fuel cells (Maghanaki *et al*., 2013; Surendra *et al*., 2014; Zahrim, 2014).

Several renewable residues have been used for biogas production which are classified into organic wastes (municipal waste, wastewater sludge, swine manure, cow manure and other related residues), energy crops (sunflower, rape, jatropha, cardoon, etc.), agricultural residues (banana stem, barley straw, rice straw, softwood spruce, etc.), agricultural crops (maize, wheat, barley, sweet sorghum, etc.) and non-conventional feedstocks (glycerol, microalgae, etc.) (Begum and Saad, 2013; Gissen *et al*., 2014; Karellas *et al*., 2010; Regassa and Wortmann, 2014; Yang *et al*., 2008).

Anaerobic digestion has been used as an effective technology for converting different renewable organic residues into biogas; which is tagged with several advantages besides energy generation, including waste stabilization, production of biofertilizer and soil conditioners, reduction of green house gas emission, non-competitiveness with food crops, decreased levels of deforestation and ease of the technology with no geographical restriction (Surendra *et al*., 2014; Parawira, 2009; Weiland, 2010).

Different microbial systems participate in transforming organic residues in a number of reactions into biogas under anaerobic conditions, these include; hydrolysis-acidogenesis, acetogenesis and methanogenesis (Antoni *et al*., 2007; Weiland, 2010; Qasaimeh *et al*., 2016). These processes proceed under different conditions including low temperature <25°C dominated by psychrophilic organisms, moderate temperatures between 25-45°C for mesophilic organisms and high temperatures from 50°C and above for thermophilic and other extremophilic species (Saidu *et al*., 2013; Sanchez *et al*., 2001).

Generally, hydrolysis as the first step has been pointed out to be the key in achieving a successful digestion process (Kim *et al*., 2003). Based on this, different pretreatment methods aimed at improving the hydrolysis have been carried out such as thermal treatment at 50-220°C, mechanical breakdown (ultrasonic, high pressure homogenization and other milling processes), chemical (acid, alkali and ozone) and biological treatments (Miah *et al*., 2005; Qiao *et al*., 2011). Ferrer *et al*. (2008) showed that methods used in enhancing the hydrolytic step, result in improvement of biogas production due to disintegration and release of organic contents making them easily accessible to microbial action during the anaerobic process. This review deals with pretreatment methods and its main goal is to give an overview of the techniques that prove effective in enhancing the biogas production during anaerobic digestion processes of organic wastes.

Biogas production using different organic wastes: Different wastes have been utilized for biogas production ranging from solids, semi-solids and liquids in form of manure, wastes and other residues obtained as byproducts of industry, agricultural farms, disposal plants, etc. Biogas from these sources could be produced in various capacities with intent of meeting different energy demands (Schroder *et al*., 2008). However, production is strongly influenced by several factors including Carbon/Nitrogen (C/N) ratio, temperature, pH, mineral composition and presence of inhibitors (Esposito *et al*., 2012; Mata-Alvarez *et al*., 2000). The use of more than one substrate (co-digestion) for biogas production has been tagged with some advantages including faster degradation rate, cost-effectiveness in terms of product formation, optimization of moisture and nutrient contents and reduction in concentration of inhibitory compounds (Divya *et al*., 2015; Luostarinen *et al*., 2009; Mata-Alvarez *et al*., 2000).

Utilization of municipal sludge for biogas production was reported by Kalloum *et al*. (2011) where the sludge was prepared to have 16 g L^{-1} of Total Solids (TS) with total flora concentration of 1.67×10^6 germs mL^{-1}. It was subjected to anaerobic digestion for 33 days, biogas production started from 7th day and reached its maximum after 26th day with about 280.31 N mL (45% methane content) based on a yield of 30 N mL of biogas mg^{-1} COD. This process resulted in the formation of digestate free of all tested pathogenic organisms with reduction of sludge COD, BOD and TS of 88, 90 and 81%, respectively.

Connaughton *et al*. (2006) carried out a comparative study in two expanded granular sludge bed-anaerobic bioreactors at 15 and 37°C using brewery waste water of 3136 ± 891 mg L^{-1} COD concentration. Following 194 day experiment, COD reduction was not significantly different between the two temperatures with a range of 85-93%. Biogas production with methane content of 50% was found when the organic loading rate was fixed at 4.47 kg m^{-3} day^{-1} for 15°C with liquid up-flow velocity of 5 m h^{-1} and at 37°C, hydraulic loading rates of 1.33 m^3m^{-3} day^{-1} was the optimum.

Co-digestion of cheese whey with dairy manure resulted in better biogas production. Kavacik and Topaloglu (2010) used two solid matter rates of 8 and 10% based on HRT of 5-20 days. Highest biogas production of 1.510 m^3 m^{-3} day^{-1} with methane content of about 60% was obtained from 8% total solid matter at HRT of 5 days and temperature of 34°C. However, removal efficiencies of 49.5, 49.4 and 54% for TS, VS and COD, respectively were found to be optimum following the HRT of 10 days under the same conditions. Similarly, mixture of equal ratio of cattle slurry and cheese whey was tested for biogas production. Methane yield of 343.43 L-CH_4 kg^{-1} volatile solid was achieved by using an Organic Loading Rate (OLR) of 2.65 g volatile solid L^{-1} day^{-1}. Overall, total biogas production was found to be 621 L kg^{-1} volatile solid at HRT of 42 days with 82 and 90% removal efficiencies of COD and BOD_5, respectively (Comino *et al*., 2012).

Cattle manure was supplemented with Palm Oil Mill Effluent (POME) for biogas production, two bioreactors labeled R1 and R2 containing cattle manure in the absence and presence of POME. The digestion process was preceded for five days using batch mode of operation followed by semi continuous operations using Hydraulic Retention Time (HRT) of 20 days. Higher biogas production was achieved in R2 with methane content of 41% compared to 18% in R1. In case of COD, R2 resulted in 10% higher reduction than R1 (Saidu *et al*., 2013). Enhanced biogas production was realized when Olive Mill Effluent (OME) was mixed with Laying Hen Litter (LHL) at a percentage dry matter of 10%. Biogas production was found to be several fold higher during the co-digestion compared to when OME was used as mono-culture. The COD conversion rates of 2.6, 2.1 and 1.94 folds were achieved for 3, 10 and 30 g L^{-1}. Thus, increase in LHL concentration to 10% resulted in 90% increment in overall biogas production (Azbar *et al*., 2008).

Kafle *et al*. (2013) studied the potential of fish waste silage prepared by addition of Bread Waste (BW) and Brewery Grain Waste (BGW) for biogas production. Following 96 days of digestion, maximum biogas production of 671-763 mL g^{-1} volatile solid with methane recovery of 441-482 mL g^{-1} volatile solid was obtained. Thus, fish waste silage digestion process was found to have significant HRTs and digestion periods of 21.0-23.8 days and 40.5-52.8 days, respectively.

Five different feed mixes containing Flushed Dairy Manure (FDM) and Turkey Processing Wastewater (TPW) were prepared by Ogejo and Li (2010) to determine the best substrate mixture for enhanced biogas production. Biogas production steadily increased from 0.072-0.8 m^3 per kg volatile solid (methane content of 56-70%) with increasing concentration of TPW and ratios of 1:1 and 1:2 FDM with TPW were found to produce biogas that can sufficiently generate electricity in a 50 kW generator for 5.5 and 9 h, respectively.

Biogas production using organic wastes holds a sustainable future based on their abundance in both developing and industrialized nations. Thus, the production process is of economic and environmental importance.

Pretreatment methods: Utilization of organic wastes for biogas production using mono-and co-digestion methods has been widely reported. Despite the multi-stage reactions associated with the production, hydrolysis as the first step is crucial and aids in increasing the overall yield. This is based on the fact that, optimization of hydrolysis step results in decomposition of complex organic matter into high amounts of monomeric and oligomeric units that can easily be utilized under anaerobic condition for generation of biogas. The target of any pretreatment methods is to make the available nutrients accessible to most microbial species which speed up biomass utilization during anaerobic digestion process (Patil *et al*., 2016).

The pretreatment processes that can be applicable in enhancing biogas production can be grouped into mechanical, thermal, chemical and biological treatments as described in the following sections. Mata-Alvarez *et al*. (2014) pointed out that vast majority of the researches associated with pretreatment of organic wastes for biogas production were devoted to mechanical, thermal and chemical methods accounting for 33, 24 and 21%, respectively. The remaining percentage could be based on combination of more than one methods.

Mechanical pretreatment: Mechanical pretreatment aids in reducing the particles of the organic residues, without generating any products that may have inhibitory effect; thus this method is associated with increase in biogas production but its major drawback is that it is an energy requiring process. Based on this, advances in milling methods show that wet milling is more preferable than dry milling process due to its higher pulverization properties with minimal energy consumption (Fuerstenau and Abouzeid, 2002). Particle size reduction by household disposer and bead mill to enhance biogas production was studied by Izumi *et al*. (2010). Following the anaerobic digestion, methane yield was found to be 28% higher in bead mill treated waste at 1000 revolutions compared to those treated with household disposer. However, increasing the revolutions of bead mill resulted in further reduction of particle size which leads to significant reduction in methane yield during the digestion process. Nah *et al*. (2000) reported the use of collision-plate at 300 kPa as a mechanical pretreatment for pilot scale anaerobic digestion of waste activated sludge. The process resulted in solubilization of organic matter with 5-7 folds increment in sCOD and soluble total organic carbon and SRT of the digester was reduced to 6 days instead of 13 days. Biogas production of 790-850 L kg^{-1} VS was obtained which corresponded with 30% VS removal efficiency.

High Pressure Homogenization (HPH) has been reported to be used as a mechanical pretreatment method for anaerobic digestion of organic sludges with ability to disrupt cells and sludge flocs, resulting in high sCOD and hydrolysis of macromolecules to their monomeric units. This method was not commonly applied for sludge pretreatment as it was widely employed to stabilize food and dairy emulsions (Nah *et al*., 2000; Zhang *et al*., 2012a, b). Some of the advantages associated with the method include high disintegration potential, minimal operational costs, ease of operation and handling with no chemical changes (Rai and Rao, 2009). The operation is generally dependent on shear stress as a result of pressure gradient build up on the sludge surfaces. The use of HPH prior to anaerobic digestion of sludge was investigated by Zhang *et al*. (2012b); the removal of volatile solids as well as COD was found to correlate well with increase in homogenization pressure. Depending on the number of cycles, 50 and 40 MPa were found to be the optima for one and two cycles, respectively and biogas production reached 3330 mL which was 115% higher than that of unpretreated sludge. Thus, HPH pretreatment led to 64% methane contents compared to 47% in unpretreated under the same conditions.

Ultrasonication has been found to be efficient in organic wastes pretreatment prior to anaerobic digestion; the process involves releasing bioavailable nutrients through hydrolysis as a result of distruption of biosolid flocs and bacterial cells which enhance nutrient solubilization as well as the overall process of anaerobic degradation (Elbeshbishy *et al*., 2011; Muller *et al*., 2009). Lehne *et al*. (2001) describe the complexity of sonication as it involves a lot of processes including chemical reactions with radicals, shearing, pyrolysis and combustion. The combined effects of these processes make ultrasonication efficient for pretreatment of organic sludges. Based on this, Pilli *et al*. (2011) developed an extensive review where he describes ultrasonication as the most effective pretreatment method for sludge and the process efficiency is solely dependent on sludge characteristics. Thus, Perez-Elvira *et al*. (2006) reported that pretreated organic wastes using ultrasonic methods resulted in soluble Chemical Oxygen Demand (sCOD) of six orders of magnitude compared to the unpretreated and this led to 10-60% enhancement in biogas production during anaerobic digestion.

Using a frequency of 20 kHz for ultrasonication at different time on leachate samples showed higher organic matter solubilization based on increment in ratio of sCOD to total COD of 63% at 600 W L^{-1} following sonication for 45 min. Anaerobic digestion of the pretreated sample led to 40% higher biogas production compared to control with methane production rate of 107 m^3 CH_4 day^{-1}. This clearly demonstrated that low frequency ultrasonication as a pretreatment step affects the overall performance of anaerobic digestion process (Oz and Yarimtepe, 2014).

In order to determine the effects of ultrasonic pretreatment on biogas production, Apul and Sanin (2010) studied three different sets of operational conditions in anaerobic digesters using both pretreated and unpretreated waste sludge. The parameters monitored were HRT and OLR which were set at 15, 7.5 and 7.5 days (HRT) and 0.5, 1 and 0.5 kg VS m^{-3} day^{-1} (OLR) for set ups 1, 2 and 3, respectively. Despite the fluctuations at early stages of operations, biogas production was apparent under steady state conditions with 49, 39 and 56% higher production than control in set ups 1, 2 and 3, respectively.

Specific energy of 500 kJ kg^{-1} TS was reported to be optimum for ultrasonic pretreatment of hog manure prior to anaerobic digestion. This was found to be sufficient for degradation of bound proteins as well as COD solubilization. Enhanced biogas production with 28% increment in methane content was observed. Based on this, low energy input was found to contribute significantly to the overall methane production rate (Elbeshbishy *et al*., 2011). Similarly, subjecting waste activated sludge to ultrasonic pretreatment at 10,000 kJ kg^{-1} TS led to a better anaerobic digestion process. Biogas production was significantly enhanced by 172.56% compared to the control; which was apparent with high sCOD generated. A considerable increase up to 758 L kg^{-1} VS was obtained when relating the biogas production with amount of volatile solid degraded (Zhang *et al*., 2013).

Castrillon *et al*. (2011) carried out batch experiments to determine the effect of co-digestion of cattle manure following its pretreatment using ultrasonication with glycerin for enhanced biogas production under temperature controlled conditions in stirred tank reactors. At the initial stage, addition of 4% glycerin to the pretreated manure led to 400% increment in biogas production at 35°C. Further increment in biogas production up to 800% was obtained when the mixture of manure +4% glycerin was subjected to sonication at 20 kHz, 0.1 kW, for 4 min. Highest biogas production was obtained at 55°C on pretreated mixture of manure +6% glycerin which yielded 348 L methane kg^{-1} COD utilized.

Based on the available literature associated with mechanical pretreatment, ultrasonication has been the most widely reported for pretreatment of wastewater, sludge and manure during anaerobic digestion processes for biogas production (Apul and Sanin, 2010; Elbeshbishy *et al*., 2011; Oz and Yarimtepe, 2014).

Thermal pretreatment: This method aids in hydrolyzing complex organic constituents of organic wastes and has been found to enhance anaerobic digestion. Li and Noike (1989) showed that pretreatment using this method results in high solubility of organic waste constituents which promote the conversion of the hydrolyzed substances under anaerobic condition to biogas through volatile organic acid production. Pretreatment of several organic wastes including cow manure, pig manure and municipal sewage sludge was studied by Qiao *et al*. (2011) using thermal method at 170°C for 1 h. Increment in biogas production of 7.8, 13.3 and 67.8% was obtained for cow manure, pig manure and municipal sewage sludge respectively compared with the control. Thus, the commonly employed temperatures for thermal pretreatment were between 60-180°C and above the upper limit of this range, compounds that slow down the digestion process may be formed (Wilson and Novak, 2009). Methane production of swine waste using this pretreatment method at 170°C and 7 bar was reported to be 35% higher compared to the control (Gonzalez-Fernandez *et al*., 2008); while improvement of biogas production by 60-70% was also reported during sludge digestion at 175°C by Haug *et al*. (1978).

Based on this, Bougrier *et al*. (2008) pointed out that thermal pretreatment can be grouped into two, where temperatures between 70 and 121°C resulted in 20-30% enhancement in biogas yield and up to 100% increment could be seen at 160-180°C.

Bougrier *et al*. (2006a) studied the effect of different thermal treatment on sewage sludge prior to digestion. The temperatures considered were 130, 150 and 170°C for 30 min. Remarkable results obtained for pretreated sludge at 150 and 170°C showed 60 and 70% COD reduction, respectively compared to 34% in the control. Thus, considering 20°C rise in temperature (from 130-150°C and to 170°C), methane yield improvement of 18 L CH_4 kg^{-1} VS which corresponds to 648 kJ kg^{-1} VS was obtained. This indicated that biogas production was highest at 170°C which could be related to higher sludge solubilization compared to other temperatures. Additionally, about two fold removal rates of total solids and volatile solids were seen in anaerobically digested pretreated sludges compared to the control and 170°C led to about 80% removal efficiency and biogas yield.

Sludge obtained from municipal waste water treatment plant was subjected to pretreatment at 70°C in order to increase the amounts of utilizable organic matter in form of Volatile Dissolved Solids (VDS) and sCOD. The effects of pretreatment periods (9, 24, 48 and 72 h) were considered which resulted in significant enhancement of VDS from 1.5 g L^{-1} VDS in the untreated sludge to 11.9-13.9 g L^{-1} VDS in 9, 24 and 48 h pretreated sludges. This shows an apparent increase in the ratio of soluble to total organic matter constituents from 5-50% after different periods of pretreatment at 70°C. Following the anaerobic digestion, difference in biogas yield was noticed after 10 days with 50% increment in 9, 24 and 48 h pretreated sludges and the total biogas yield for the 37 day assay revealed 30 and 15% increments for 9 and 24-48 h pretreatments, respectively. Overall pretreatment time of 72 h did not show a better result which could be linked to presence of some inhibitory compounds associated with volatile fatty acids (Ferrer *et al*., 2008).

Similarly, Mottet *et al*. (2009) carried out sludge pretreatment at various temperatures (110, 165 and 220°C) and maximum VDS and sCOD of 24 and 27% were obtained in 220°C pretreated sludge; however biodegradability and methane yield were found to be lower than the control which could be related to production of recalcitrant compounds including Amadori and melanoidins. The best pretreatment was that of 165°C, where VDS of 15% and sCOD of 18% were observed with significant increase in biodegradability under anaerobic process from 47-61%. Methane yield was found to be 30% higher in 165°C pretreated sludge (215 mL CH_4 g COD^{-1}) than the control (165 mL CH_4 g COD^{-1}).

In another development, freezing and thawing of sludge lead to cellular disruption accompanied by releasing constituent materials in the supernatant as reported by Ormeci and Vesilind (2001). This motivated, Montusiewicz *et al*. (2010) to study their effect on sewage sludge during anaerobic process. A remarkable reduction of 12, 16.1 and 16.9% in total COD, TS and VDS, respectively was observed, while sCOD was found to be two times higher in pretreated sludge by freezing and thawing than the control. Biogas production was enhanced by this method with 1.31 m^3 kg^{-1} VS and this value was 1.5 times higher than what was obtained in unpretreated sludge. Thus, several reports have shown the effects of thermal pretreatment prior to anaerobic digestion for improving the biogas production as indicated in Table 1.

Table 1: Some of the thermal pretreatment studies reported for organic sludge

Thermal pretreatments	Effects	Biogas production	References
70-90°C (15-60 min)	sCOD increment in 60 min pretreated (2.9 folds at 70°C, 20.5 folds at 80°C and 25.6 folds at 90°C); increment in total VFA in 60 min pretreated (14.3 folds at 70°C, 17 folds at 80°C, 36.6 folds at 90°C)	2 and 11 folds increase in 60 min pretreated sludge at 80 and 90°C, respectively	Appels *et al.* (2010)
70-190°C (3 h for <100°C and 20 min for >100°C)	Increase in biodegradability from 26% for the control to 43% in pretreated at 190°C. sCOD increase from 7.41-19.31 g L^{-1} and 3.9 fold increase in VFA after treatment at 190°C	64% improvement with a production of 4963 L CH_4 m^{-3} manure	Carrere *et al.* (2009)
170°C for 60 min	COD and TS removal of 70.7 and 59.3% against 43.9 and 27.3%, respectively for the control	61% higher yield with a value of 142 dm^3 CH_4 kg^{-1} COD_{feed}	Valo *et al.* (2004)
121°C (30 min)	2.2 fold increase in sCOD (i.e., 4900 mg L^{-1} against 2250 mg L^{-1} of the control) with VS reduction of 32.1%	32.4% higher yield with a value of 4843 L m^{-3} WAS	Kim *et al.* (2003)
70°C (9 h)	Increment in degree of disintegration based on the ratio of filterable VS to total VS of 751±36% and volatile fatty acid increment of 43±5%	57.6% higher yield compared to control	Climent *et al.* (2007)
120°C (30 min)	3.6 and 8 folds increase in VFA concentration and sCOD	22% higher yield with specific methane rate of about 24 mL g^{-1} VS day^{-1}	Jeong *et al.* (2007)
25, 50 and 70°C (48 h)	COD solubilization of 23.13% at 50°C and several folds increase in sCOD	11% higher yield with methane content in biogas of 69%	Nges and Liu (2009)
220°C (10-30 sec)	55% of total solids solubilization	80% improvement with 200% increase for the initial 1-2 days	Zheng *et al.* (1998)

Besides the commonly employed thermal pretreatment, microwave pretreatment has been found to be effective in organic waste stabilization as well as biogas production. This involves the use of electromagnetic radiation between the wavelength range of 1 mm to 1 m which is equivalent to 300 GHz-300 MHz oscillation frequency and a frequency of 2450 MHz (12.24 cm wavelength) with energy of 1.02×10^{-5} eV could be sufficient for pretreating waste activated sludge (Eskicioglu *et al*., 2007; Mudhoo and Sharma, 2011). This method has some advantages including fast heating and penetration, elimination of pathogens, ease of handling and control, efficient sludge dewaterability and sludge reduction (Jones *et al*., 2002) and these make it more effective than conventional thermal technique.

The efficiency of microwave irradiation was explained based on two mechanisms; thermal effect, where temperature increase results in interaction of the electric field with dipolar molecules (water, proteins, fats and other organic complexes) causing molecular rotation accompanied by internal pressure build up which generate internal heating as well as cellular destruction. Alteration of polarized side chains of macromolecules caused by alternating electric field of microwaves resulting in disruption of intermolecular interactions which affect the secondary and tertiary interactions is considered as non-thermal effect (Appels *et al*., 2013; Eskicioglu *et al*., 2007; Solyom *et al*., 2011).

Eskicioglu *et al.* (2007) studied the effect of microwave irradiation on waste activated sludge within a range of 50-96°C, no significant difference was observed in terms of sCOD, protein and polysaccharide solubilization between the pretreated and control using conventional heating. An improved biogas production was observed in pretreated sludge at 96°C over the control which indicated the contribution of non thermal effect of microwave irradiation in anaerobic digestion process with 16±4% higher yields compared to the control after 15 days of digestion.

Moreover, using continuous flow anaerobic sludge digesters, microwave pretreated sludge showed 3.6 and 3.2 folds increment in sCOD to total COD ratios at 1.4 and 5.4 total solids, respectively with 17.0% improvement in biogas production compared to control following a 34 day digestion process (Eskicioglu *et al*., 2006). Similarly, Eskicioglu *et al.* (2009) irradiated waste activated sludge at 50-175°C and observed that increasing trends existed between soluble to total COD as well as soluble solids to total solids and temperature. The proportions of 24, 28 and 35% for soluble to total COD and 19, 21 and 32% for soluble solids to total solids with corresponding temperature of 120, 150 and 175°C, respectively were recorded. Despite the initial inhibition of methane production in the first 9 days, sludge irradiated at 175°C showed better performance with 31% higher biogas production than the control after 18 days of digestion.

Thus, organic matter solubilization and biogas production were used to study the effect of microwave absorbed energy in sludge samples; when the energy was 0.54 kJ mL^{-1} at 1000 W, higher solubilization effect was found which yielded 7.1% higher methane content compared to the control. Further improvement in methane production of 15.4% was obtained when the energy was increased to 0.83 kJ mL^{-1} (Solyom *et al*., 2011). Park and Ahn (2011) reported the effect of microwave pretreatments on mixtures of primary and secondary sludges during the anaerobic digestion, which resulted in 3.2 folds increment in sCOD to total COD ratio and VS removal of 41% with daily biogas production of 53% at reduced HRT of 5.

Thermal pretreatment using both conventional and microwave methods aids in efficient solubilization of sludge, which shortens the rate limiting steps (hydrolysis) during anaerobic digestion and overall results in higher biogas yield as indicated in several researches reported herein.

Chemical pretreatment: This method is effective in breakdown of organic constituents through the action of acids, alkali and oxidants. Among the chemical based methods, oxidation (ozonation and peroxidation) has been found useful in pretreatment resulting in sludge solubilisation. A dose dependent relationship exists between sludge solubilization and oxidant concentration up to a certain limit. Thus, ozonation/peroxidation being oxidative process tends to show higher rate of sludge biodegradation with compromised biogas yield (Carrere *et al*., 2010; Yeom *et al*., 2002). Acid and alkaline methods are mostly applied in combination with other methods for sludge solubilization.

Oxidation of both organic and inorganic compounds of sludge can be achieved in the presence of ozone; this leads to cellular disruption, flocs disintegration, high COD solubilization and under extreme condition, mineralization occurs. Depending on the intended applications, ozone concentration of 0.05 and 0.5 g O_3/g TS has been found to be adequate for the pretreatment of sludge (Kameswari *et al*., 2011; Tyagi and Lo, 2011; Yeom *et al*., 2002). Bougrier *et al*. (2006b) found that biogas yield during digestion of ozonized sludge correlated with increase in ozone concentration up to 0.15 g O_3/g TSS, followed by a sharp reduction.

Weemaes *et al*. (2000) studied the effect of ozone pretreatment prior to anaerobic digestion of sludge using 0.1 g O_3/g COD. About 38% of the organic constituents were oxidized and 29% were solubilized which lead to changes in VSS compositions of the ozonized sludge. The digestion process resulted in 1.8 and 2.2 increments in methane yield and rate respectively compared to the control.

Three reactors operated at SRT of 25 days were fed with different ozonized sludge pretreated at 2.65, 1.33 and 0.66 mg O_3/g VSS and a control reactor was also used which was fed with unpretreated sludge. Biogas production was found to be highest in ozonized sludge treated at 1.33 mg O_3/g VSS with more than 200% increment compared with the control. Also, 33% enhancement in biogas production was found in 0.66 mg O_3/g VSS (Ak *et al*., 2013). Similarly, 20 mg O_3/g per TSS was found to be adequate for higher sludge solubilzation with 28 and 17% improvement in daily biogas production in reactors operated under mesophilic and thermophilic conditions, respectively when compared with the respective control (Carballa *et al*., 2007).

Furthermore, peroxidation involving the use of H_2O_2 activated by iron salts was reported to disentegrate sludge and rupture the cellular components which lead to increased concentration of sCOD. Three oxidative pretreatment were carried out using Fenton peroxidation, dimethyldioxirane (DMDO) and peroxymonosulphate (POMS) methods on activated sludge to determine their rate of solubilization as well as biogas production. The breakdown of organic matter was verified by monitoring the level of DS, COD and BOD. The POMS and DMDO had higher solubilzation effects than Fenton peroxidation. Also, 2.5 and 2 folds increment in terms of biogas production were observed in sludge pretreated with DMDO and POMS, respectively. Comparatively low biogas yield was recorded for peroxidation but the methane contents in all the three treatments were between 65 and 70% (Dewil *et al*., 2007).

Another oxidant with good potential is peracetic acid, which reacts with organic matter to form hydroxyl radicals that further reacts with other components. The process does not produce toxic byproducts instead it dissociates to water and acetic acid which can contribute its carbon skeleton for biogas production (Appels *et al*., 2011). Biogas enhancement of 21% was reported by Appels *et al*. (2011) with good sludge disintegration and organic matter solubilization compared with the control.

Thus, oxidation process (ozonation, peroxidation and peracetic acid) is capital intensive with good sludge solubilization effect; however, higher ozonation results in the formation of soluble compounds which may have deleterious effect when discharged into the environment, while low pH, proper handling as well as specialized equipment associated with peroxidation based on its corrosiveness limit their applications. As such, the benefits as well as cost implication should be critically looked at before adopting any process on a large scale.

Acid and alkali pretreatments have been used to solubilize sludges in an easy way with little or no energy demand and overall the process may result in pathogen free digestate. However, extreme pH is required in both cases for efficient solubilization and this to some extent is a drawback to this method as further treatment involving neutralization may be required.

Devlin *et al*. (2011) showed that pretreatment of waste activated sludge using HCl (pH 1-6) led to higher solubilisation of macromolecules and COD; based on this, pH 2 was selected

Table 2: Some of the biogas improvement by combined pretreatment methods

Treatments	Process	Yield	References
Microwave irradiation (160°C) and Alkaline (pH 12)	Semi-continuous process (HRT of 15 days) under mesophilic condition (37°C)	43.5 and 55% improvements in daily total gas and methane productions, respectively	Dogan and Sanin (2009)
Microwave (2,450 MHz, 800 W) and Ultrasonication (0.4 W mL^{-1})	Stirred batch anaerobic reactors (HRT of 17 days) under mesophilic condition (37.5°C)	Methane production (146 mL g^{-1} COD) was 4.8 and 9 folds higher than the respective control of ultrasonication and microwave, respectively	Yeneneh *et al.* 2013)
Alkaline (4 mol L^{-1}) and high pressure homogenization (60 MPa)	Batch anaerobic digestion under mesophilic (35°C) condition	60 and 68% increment in biogas and methane content, respectively	Fang *et al.* (2014)
Thermo-alkaline (80°C, pH 8)	Semi-continuous process (HRT of 21 days) under mesophilic condition (35°C)	58% increase in biogas production	Carrere *et al.* (2012)
Thermo-alkaline (190°C, pH 10)	Zipperclave agitated anaerobic reactor under mesophilic temperature (35°C)	Biogas improvement of 78%, with 7015 L CH_4 m^{-3} manure	Carrere *et al.* (2009)
Thermo-alkaline (60°C, pH 12)	Batch and semi-continuous process (SRT of 15 days) under mesophilic condition (35°C)	51 and 103% higher biogas production than control in batch and semi-continuous processes, respectively	Rani *et al.* (2012)
Thermo-alkaline (90°C, pH 11)	Batch anaerobic digestion under mesophilic (35±2°C) condition	52.78% biogas production with a yield of 605 L kg^{-1} VS	Xu *et al.* (2014)
Electro-chemical (5 V, pH 9.2)	Batch anaerobic digestion under mesophilic (35±1°C) condition	20.3% improvement in biogas production with methane yield of 149.72±4.63 mL CH_4 g^{-1} COD	Zhen *et al.* (2014)
Electro-chemical (20 V, 0.6% (v/v) NaClO, pH 8)	Batch anaerobic digestion under mesophilic (35±2°C) condition	63.38% biogas production with a yield of 647 L kg^{-1} VS compared to the control	Xu *et al.* (2014)

to be the best. Following a batch digestion, biogas production of 400 mL per gram VS was recorded after 13 days and the same amount was obtained in untreated after 21 days. Using semi continuous process, the HRT further reduced to 12 days; 10.8% higher methane yield per g VS added and 14.3% higher methane yield per g COD added were obtained in comparison with the control.

Alkaline pretreatment was studied by Lin *et al.* (1997) where different concentrations of NaOH were used. Four anaerobic digestion set ups were prepared containing 20 meq L^{-1} NaOH pretreated sludge at 1% TSS, 40 meq L^{-1} NaOH pretreated sludge at 1% TSS, 20 meq L^{-1} NaOH pretreated sludge at 2% TSS and a control where unpretreated sludge was used. Reactors fed with the pretreated sludges showed better performance with higher COD removal rate. Biogas production was found to be highest in 20 meq L^{-1} NaOH pretreated sludge at 2% TSS with a yield of 163% in comparison with the control.

Thus, the alkali used in sludge solubilization has been ranked by Kim *et al.* (2003) as NaOH>KOH>$Mg(OH)_2$>$Ca(OH)_2$. Lin *et al.* (2009) reported about 83% improvement in sCOD with high concentration of VFA in 8 g NaOH/100 g TS_{sludge}. Biogas production was found to be 183.5% higher with 0.32 m^3 CH_4 kg^{-1} $VS_{removal}$ than the control.

Chemical Pretreatment involving the use of alkali and acid are mostly used in combination with other treatments techniques as indicated in the following section.

Combined pretreatment: This involves the use of more than one pretreatment method where their combined effects result in better sludge solubilization which in turn leads to higher biogas production. Several studies reported the combination of physical (mechanical, thermal) with chemical (acid, alkali, ozone) methods and the results seem to be attractive. Some of the combined pretreatments reported in the literature have been presented below and Table 2 shows the synergistic effects of the pretreatments in enhancing the biogas production.

Systematic combination of thermal and chemical methods was found to be appropriate for enhanced sludge disintegration and biogas production as reported by Kim *et al.* (2003). Out of the four pretreatment methods tested on Waste Activated Sludge (WAS), thermo-chemical method at 121°C for 30 min and 7 g NaOH L^{-1} led to the maximum biogas production of 3367 L CH_4 m^{-3} WAS which was 38% higher than the control.

Various sludge pretreaments were carried out at temperatures of 50-90°C and pH of 8-11. A linear relationship was found between the rate of sludge disintegration and the applied thermochemical treatments. The best pretreatment condition was found to be 90°C and pH 11, which resulted in about 46% reduction in volatile suspended solids with methane content of 0.28 L CH_4 kg^{-1} VSS (Vlyssides and Karlis, 2004).

Thermo-chemical method for pretreating activated sludge revealed high sCOD solubilization of 27.7, 31.4 and 38.3% corresponding to 25, 35 and 55°C, respectively after 4 h of incubation when the concentration of alkali was kept at 45 meq NaOH L^{-1}. Following anaerobic digestion based on 20 day HRT, the pretreated sludge at 25, 35 and 55°C led to methane content of 274, 286 and 310 mL CH_4 g^{-1} VS, respectively; which were found to be 66, 73 and 88% higher than the control (Heo *et al*., 2003).

Shehu *et al*. (2012) reported the use of Box-Behnken design to optimize the sludge pretreatment by thermo-alkaline method for improved biogas production. The developed quadratic model revealed the highest sludge disintegration of 61.45% and biogas yield of 36% higher than the control at optimum temperature of 88.50°C and NaOH of 2.29 M (24.23% w/w total solids). The adequacy of the model was confirmed based on its coefficient of determination (R^2) of 99.5%.

Of recent, electrochemical method has been applied in the pretreating sludge prior to anearobic digestion and has shown a high level of flexibility, good sludge solubilization and environmental friendliness with minimal temperature requirement (Song *et al*., 2010; Xu *et al*., 2014; Zhen *et al*., 2014).

Thus, combined pretreatment methods are advantageous in enhancing sludge solubilization, sludge sanitation, dewaterability and anaerobic digestion. However, insight in their wide application and economic analysis will prove their effectiveness as some of them are still based on laboratory proof of concepts.

Biological pretreatment: This method has been advocated as a result of its environmental friendliness, where different microbial systems work synergistically in hydrolyzing complex organic matter thereby improving anaerobic digestion (Gupta *et al*., 2012).

In case of organic sludge, extracellular enzyme catalyzed reactions within the system lead to sludge disintegration and solubilization. Although this process is environment-friendly and less capital intensive compared to other methods; however the process requires longer time and controlled environmental conditions for microbial growth.

Hasegawa *et al*. (2000) reported the use of thermophilic aerobic bacteria to enhance the sludge disintegration prior to anaerobic digestion. The isolate SPT2-1 obtained from aerobic digester grow under thermophilic condition (60-70°C) with good pH tolerance of 5.0-8.5 showed increased sludge solubilization in terms of volatile suspended solids (25-30%) by secreting hydrolytic enzymes (e.g., protease, amylase, etc.) and biogas production was found to be 1.5 fold compared to the control.

Addition of *Bacillus* sp. to enhance anaerobic digestion showed about 95% increment in methane production compared to the control. Similarly, addition of some micronutrients (Fe^{2+}, Ni^{2+}, Co^{2+} and Mo^{2+}) together with *Bacillus* sp. further improved the methane production by 167%. Following the statistical design, the actual concentrations that resulted in higher methane yield were 4.5, 0.75, 0.45, 0.09 and 12 mg g^{-1} VS for Fe^{2+}, Ni^{2+}, Co^{2+}, Mo^{2+} and *Bacillus* sp., respectively (Noyola and Tinajero, 2005).

Singh *et al*. (2001) studied the effects of Microbe Activating Technology (MAT) where two microbial enhancers (Aquasan® and Teresan®) were applied to cattle dung for anearobic digestion. Different concentrations of Aquasan® (10, 15 and 20 ppm) were applied to cattle dung prior to digestion and biogas yield was found to be 45.1-62.1 L kg^{-1} dry matter. Following the incubation of 15 days, addition of Aquasan® (15 and 20 ppm) increased the biogas yield by 15-16%. Thus, maximum biogas production was found to be 39 and 55% higher with single and double dosage of 15 ppm of Aquasan®. In case of Teresan® at 10 ppm, biogas yield was 34.8% higher than the control.

Aerobic Thermophilic (AT) bacteria which was found to have close similarity with *Geobacillus thermodenitrificans* was used to pretreat sludge prior to digestion. About 21% reduction in volatile solids was obtained with 2.2 folds increment in biogas production (Miah *et al*., 2005). Bacterium B4 with potent hemicellulose degrading potential led to 30% improvement in biogas potential of cattle manure as shown by Angelidaki and Ahring (2000). Also, a significant improvement in methane yield of 1100.46 mL g^{-1} VS, which was 280% higher than the control was reported based on biological-physicochemical pretreatment method. This was based on ultrasonication for 10 min, citric acid of 500 mg L^{-1} and inoculation of *Bacillus* sp. at 9 wt% prior to anaerobic digestion of oily wastewater sludge as reported by Peng *et al*. (2014).

Generally, pretreatment using this method is found to be environmental friendly with minimal energy consumption compared to other techniques but offensive odor generation with limited waste reduction is one of its major drawbacks.

Enzymatic pretreatment: This is one of most promising biological pretreatment method in which the rate of hydrolysis of organic waste is further enhanced prior to the digestion process. The enzyme based pretreatment in solubilizing sludge starts immediately within the system unlike microbial process that requires acclimatization time. However, this process is cost intensive which is its major drawback.

Biolysis® E (commercialised by Ondeo-Degremont (Suez)) made up of different enzyme system (proteases, amylases, lipases) shows higher solubilization effect with 40-80% reduction of sludge (Deleris *et al*., 2003). Mayhew *et al*. (2003) studied the enzymatic hydrolysis of waste activated sludge, where the hydrolyzed sludge was found to be almost free from pathogens; and 10% enhancement in biogas production was recorded using retention time of 2 days at 42°C. Additionally, Parawira (2012) reported that lipase catalyzed hydrolysis of lipid-rich sludge prior to anaerobic process enhanced both sludge disentegration and methane production.

Thus, using enzymatic pretreatment for biogas production holds a promising future, but this can only be a reality if researches are tailored towards producing cheap and genetically engineered enzymes.

CONCLUSION

Several pretreatment methods of organic wastes prior to anaerobic digestion have been reported, these include mechanical, thermal, chemical, biological and hybrid (combination of more than one method) methods. Each of these methods is targeted towards enhancing the solubilization and distentegration of organic components of the waste which in effect lead to improvement in anaerobic digestion process. Biogas production is one of the major benefits of the process and depending on the employed methods; success associated with waste dewatering, pathogen elimination, waste reduction, biofertilizer and conditioners production is achievable. Different pretreatment methods have advantages as well as disadvantages but operational cost and energy consumption could play significant roles in selection process for large scale application. Thus, economic analysis including the cost of operation and the benefits derived in form of biogas, waste minimization and treatment should be the watchword.

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