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SLUDGE TREATMENT TO INCREASE BIOGAS PRODUCTION

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SUMMARY

I denna studie, sammanfattas existerande effektiva metoder att öka biogasproduktionen från behandling av kommunalt avloppsslam.

I avhandlingen redogörs först detaljerat processen för produktion av biogas och sedan för flaskhalsar i produktionen av biogas vid rötning i kommunal slamhantering. Därefter redovisas befintliga metoder inklusive termisk förbehandling, kemisk förbehandling, termokemisk förbehandling, mekanisk förbehandling och andra behandlingar som enzymatiska hydrolys, mikrovågsförbehandling, anoxisk gasflotation liksom termooxidativ behandling.

Slutligen jämförs metoderna när det gäller effektivitet i slamupplösning, driftkostnad, nackdelar och fördelar.

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CONTENTS

ABSTRACT

This paper presents a review of the main pretreatment methods which have the potential to increase biogas production in anaerobic digestion process. The methods include thermal, oxidative, thermochemical, mechanical (ultrasonic, grinding, high pressure homogenization) as well as other methods such as enzymic hydrolysis and so forth. Emphasis is mainly put on their impact on biogas production. All these methods can enhance biogas production to some extent, but the energy required and the operation cost varied. The paper displayed the interesting literatures which compare the effect on biogas production between pretreated and raw sludge, and also put forward the advantages and disadvantages of each pretreatment method. There is no conclusion about which method is the best. Further research has to be done for a better outcome.

Keywords: waste activated sludge; anaerobic digestion; biogas production; pretreatment; energy.

INTRODUCTION

Biogas, as a renewable energy, can be produced from a variety of organic raw materials and utilized for various energy services, such as heat, combined heat and power or as a vehicle fuel. Biogas can be produced by anaerobic digestion or fermentation of biodegradable materials such as biomass, manure, sewage, municipal waste, green waste, plants material and energy crops (Wikipedia, 2009). Emphasis is laid on sludge from municipal wastewater treatment plants in this paper. As we know, large amounts of waste activated sludge, containing organic and mineral components, are produced by municipal and industrial wastewater treatment plants. Most relevant is municipal solid waste, with a daily production in Europe of about 400,000 tons (Mata-Alvarez *et al.*, 2000). Sludge handling represents a bottleneck in wastewater treatment plants, due to environmental, economic, social and legal factors. If handled properly, sludge can be a valuable resource for renewable energy production and a source of nutrients for agriculture.

The characteristics of sludge vary widely from relatively fresh faecal materials generated in bucket latrines to sludge which has undergone bacterial decomposition for over a year in a double pit latrine (UNEP, 2010). The treatment required is therefore dependent on the characteristics of the sludge. However, the general process comprises thickening, digesting, further stabilizing and sludge disposal. The process flowchart of sludge processing steps is shown in Fig. 1. A first step is its thickening by gravity, flotation or belt filtration. In doing so, the amount of sludge can be reduced to as little as a third of its initial volume. The separated water is recycled to the influent of the wastewater treatment plants (WWTP). Subsequently, the pre-treatment with varied methods including mechanical, biological and chemical pre-treatment is accomplished to enhance the dewaterability and digestibility of sludge. Followed is the crucial step: digestion. The most common treatment options include aerobic digestion, anaerobic digestion and composting. Among these biological treatments, anaerobic digestion is frequently the most cost-effective, due to the high energy recovery linked to the process and its limited environmental impact (Mata-Alvarez *et al.*, 2000). In fact, more than 36,000 anaerobic digesters are in operation up to 1998 (Tilche & Malaspina, 1998). With AD playing an important role for its ability to further transform organic matter into biogas (60-70 vol% of methane, CH_4), thereby the amount of final sludge solids for disposal is reduced, most of the pathogens are destroyed and possible odour problems associated with residual putrescible matter are limited.

Biogas is currently produced mostly by digestion of sewage treatment sludge, with minor contributions from fermentation of gasification of solid waste or of lignocellulosic material (process currently being further developed). The typical details of biogas are given in Table 1 (Steinhauser, 2008). It is considered an important future contributor to the energy supply of Europe, although upgrading is needed. The annual potential of biogas production in Europe is estimated in excess of 200 billions m^3 (Lise *et al.*, 2008). In today's energy demanding life style, biogas as the typical renewable as well as eco-friendly new energy source will replace fossil fuel inevitably. Hence, how to increase biogas production is a problem of major concern in terms of environment, finance and technology. The objective of this paper is to present efficient and effective methods of increasing biogas production in anaerobic digestion of waste activated sludge treatment process.

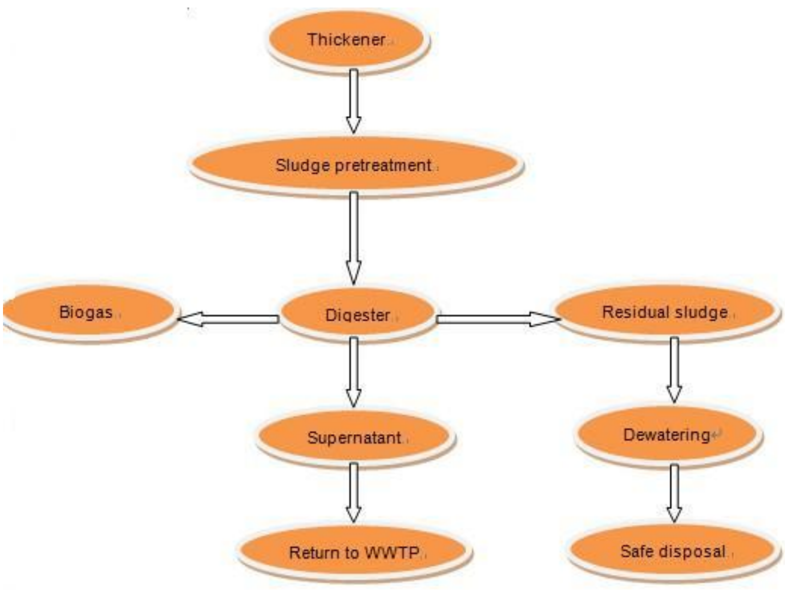

Fig. 1 Process flowchart of the sludge processing steps

Table 1 Typical details of biogas

Composition	55-70%methane, 30-45%carbon dioxide, traces of other gases
Energy content	6.0-6.5kWm^{-3}
Fuel equivalent	0.6-0.65L oil/m^{3} biogas
Explosion limits	6-12%biogas in air
Lgnition temperature	650-750 ºC
Critical pressure	75-89 bar
Critical temperature	-82.5 ºC
Normal density	1.2kgm^{-3}
Odour	Bad eggs (the smell of hydrogen sulphide)

BACKGROUND

Anaerobic digestion

Anaerobic digestion (AD) is a series of process in which microorganisms break down biodegradable material in the absence of oxygen, used for industrial or domestic purposes to manage waste and/or to release energy (Wikipedia, 2010). The main features of AD process are mass reduction, biogas production and improved dewatering properties of the treated sludge. There are four key biological and chemical steps of AD process: hydrolysis, acidogenesis, acetogenesis and methanogenesis as shown in Figure 2.

In most cases sludge contains lots of large organic polymers. In order to access the energy potential of the materials, the long chains must firstly be broken down to their smaller components such as sugars being readily available for other bacteria. This process is so called hydrolysis. The hydrolysis step degrades both insoluble organic material and high molecular weight compounds such as lipids, polysaccharides, proteins and nucleic acids, into soluble organic substances (e.g. amino acids and fatty acids). The components formed during hydrolysis are further split during acidogenesis, the second step. Volatile fatty acids are produced by acidogenic (or fermentative) bacteria along with ammonia, carbon dioxide, hydrogen sulphide and other

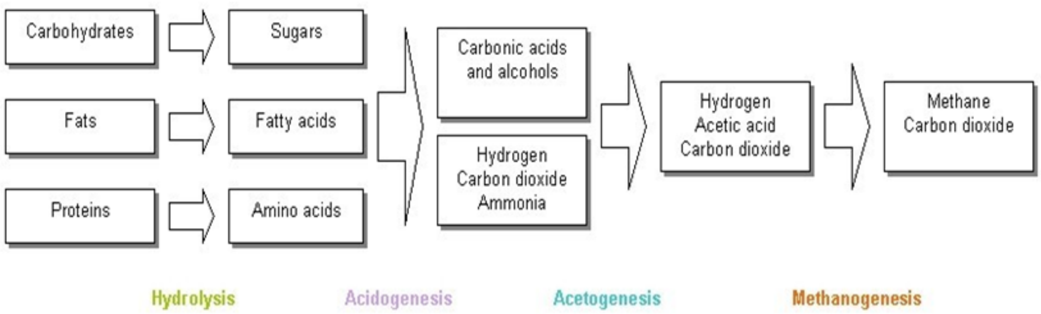

Fig. 2 The key stages process stages in anaerobic digestion.

by-products (Lise *et al.*, 2008). The third step is acetogenesis, where the carbonic acids and alcohols are further digested by acetogens to produce mainly acetic acids as well as hydrogen and carbon dioxide. Finally, methanogenesis produces methane by two groups of methanogenic bacteria: the first group splits acetate into methane and carbon dioxide and the second group uses hydrogen as electron donor and carbon dioxide as acceptor to produce methane.

Sludge from municipal wastewater treatment plant

Sludge generated from municipal wastewater treatment plants are mainly primary sludge and activated sludge. The end-product after handling the two types of sludge through anaerobic or aerobic digestion is digested sludge. Table 2 shows values of gas production from primary sludge and activated sludge cited by Brown *et al.* (2003). It's inconclusive to provide the methane content of the gas production here due to lack of ample literature.

Primary sludge

Primary is also called raw sludge which comes from the bottom of the primary clarifier. Primary sludge is easily biodegradable since it consists of more easily digestible carbohydrates and fats, compared to activated sludge which consists of complex carbohydrates, proteins and long chain hydrocarbons (Gray *et al.*, 2007). So biogas is more easily produced from primary sludge.

Activated sludge

Activated sludge is also called excess sludge or waste activated sludge which comes from the secondary treatment. It's a result of overproduction of microorganisms in the activated sludge process. The content of activated sludge was just mentioned above. Activated sludge is more difficult to digest than primary sludge.

Digested sludge

After anaerobic digestion of primary and activated sludge the residual product is digested sludge. The digested sludge is reduced in mass, less odorous, safer in the aspect of pathogens and more easily dewatered than the primary and activated sludge (Anders, 2005).

Table 2 Gas production from primary sludge and activated sludge

Reference	Gas production (mL/g VS)	
	Primary sludge	Activated sludge
Sato *et al*. (2001)	612	380
Speece (2001)	362	281
Rittmann & McCarty (2000)	375	275

SLUDGE PRE-TREATMENT FOR INCREASED BIOGAS PRODUCTION

Introduction

Evidently, anaerobic digestion has a great future amongst the biological technologies of sludge treatment in view of biogas generation as well as reducing solids mass. However, the low overall biodegradation efficiency of the sludge solids and long retention times (20-30 days) result in only moderate efficiencies.

In anaerobic digestion, the biological hydrolysis is identified as the rate-limiting step (Ghyoot & Verstrate, 1997). Most soluble organic materials which can be converted into biogas are produced during hydrolysis process. Consequently, the biogas production depends for the most part on the biodegradability and hydrolysis rate (E1 & H.E., 2003). Biogas production can thus be improved by several pretreatments in order to lyse sludge cells further to facilitate hydrolysis. In this step, both solubilization of particulate matter and biological decomposition of organic polymers to monomers or dimers take place. That is, cell walls are ruptured and extracellular polymeric substances are degraded resulting in the release of readily available organic material for the acidogenic micro-organisms. Thermal, chemical, biological and mechanical processes, as well as combinations of these, have been studied as possible pre-treatments cause the lysis of or disintegration of sludge cells permitting the release of intracellular matter that becomes more accessible to anaerobic microorganisms. This fact improves the overall digestion process velocity and the degree of sludge degradation, thus reducing anaerobic digester retention time and increasing methane production rates (Muller, 2000). The paper will provide a series of literature reviews concerning optimum conditions to obtain enhanced biogas production in varied pre-treatments of sludge hereafter.

Thermal pre-treatment

It has been known for many years that a thermal pretreatment can improve the degradability of sludge. While the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected from the enzymatic hydrolysis by the cell wall. Heat applied during thermal treatment destroyed the chemical bonds of the cell wall and membrane, thus makes the proteins accessible for biological degradation. Maximum biodegradability, in percentage, meaning the maximum percentage of substrate COD that is converted to methane, was calculated according to El-Mashad *et al.* (2004). So that biodegradability can serve as an indicator for measuring the biogas production.

Thermal pretreatment has been studied using a wide range of temperatures ranging from 60 to 270 ºC. In practice, the optimum temperature is in range of 160-180º C and treatment times from 30 to 60min. pressure associated to these temperatures may vary from 600 to 2500 kPa (Weemaes & Zeeman, 1998). Various experiments and research of thermal pretreatment have been done to proclaim this conclusion.

Li and Noike (Li & Noike, 1992) showed that optimum temperature in terms of 33% volatile suspended solids

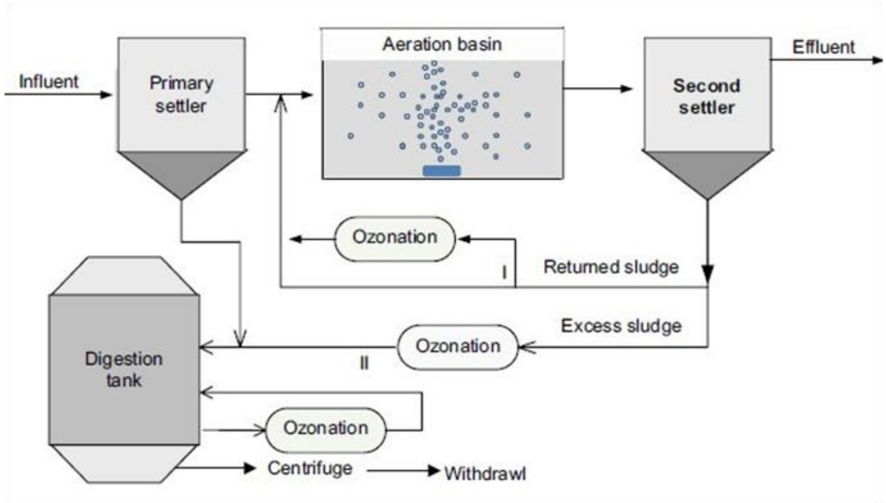

Fig. 3 Application of ozonation for sludge reduction.

degradation increased and 100% methane production was 170 °C and contact time was 60min. No further improvement for longer contact times. This is in line with the findings of Gavala *et al.* (2008) who concluded that temperature and duration of the optimum pretreatment depend on the nature of the sludge: the greater the proportion of difficult hydrolyzing biological sludge substrates, higher the intensity of pretreatments needed.

Bougrier *et al.* (2006) compared the thermal pretreatments (130 ºC, pH=10, 150 ºC and 170 ºC during 30min) performance of waste activated sludge collected from urban wastewater plants with untreated sludge samples. The results indicated that there was positive effect on solubilization rates and methanization when thermal pretreatment was added. Particularly, the 170 ºC treatment led to comparable results in anaerobic digestion performance increase: about 80% improvement in removal of matter and in biogas yield.

Haug and co-workers (2002) worked on thermal treatment at lower temperatures in order to improve dewaterability as well as digestibility and at the same time avoid the problems that occurred with higher temperature thermal pretreatment. They showed that the largest effect on digestibility was for activated sludge was at 175ºC. This temperature was about the limit for digestibility before digestion was inhibited (presumably because of the formation of inhibitory and/or refractory compounds). At 175 ºC, digestion of the thermally pretreated sludge resulted in an increase of 60-70% in methane production over not pretreated sludge. Higher temperatures led to decreased gas production.

In general, thermal pretreatment of waste activated sludge can considerably increase methane production for mesophilic anaerobic digestion and to a lesser extent for thermophilic anaerobic digestion, for that thermophilic digestion is already more efficient at volatile suspended solids reduction and methane production as compared with mesophilic digestion,

Table 3 The effect of thermal pretreatment on biogas production

Sludge	Treatment conditions	AD conditions	Result
Activated sludge (haug et al., 1978)	175 ºC 30 min	CSTR HRT: 15 days 35 ºC	Increase of CH4 production (+62%)
Activated sludge (Stuckey & McCarty, 1978)	175 ºC 60 min	Batch 25 days 35ºC	Increase of CH4 production (+42%)
Activated sludge (Y.Y. & Noike, 1992)	175 ºC 60 min	CSTR HRT: 5 days 35 ºC	Increase of gas production (100%)
Activated sludge (Fjordside, 2001)	160 ºC	WWTP 45,000 PE CSTR HRT: 15 days	Increase of biogas production (+60%)
Digested mixed Sludge (Dohanyos et al., 2004)	170 ºC 60 s 0.8 MPa	Batch 20 days	Increase of biogas production (+49%)
Activated sludge (Valo et al., 2004)	170 ºC 60 min	Batch 24 days 35 ºC	Increase of biogas production (+45%)
	170 ºC 60 min	CSTR HRT: 20 days 35 ºC	Increase of CH4 production (+61%)
	170 ºC 30 min	Batch 24 days 35 ºC	Increase of CH4 production (+76%)
Activated sludge (Bougrier et al., 2006)	170 ºC 30 min	CSTR HRT: 20 days 35 ºC	Increase of CH4 production (+51%)
Activated sludge (Fernandez et al., 2008)	170 ºC 30 min 7 bar	Batch	Increase of CH4 production (+50%)
	170 ºC 30 min 7 bar	Continuous HRT: 12 days	Increase of biogas production (+40-50%)

hence reduces benefits of pretreatment. However, some researches on combination of low temperature (<100 ºC) pretreatment prior thermophilic digestion also have been done and the effects are notable.

Climent *et al.* (2007) investigated the thermal pretreatment at low temperatures between 70 ºC to 134 ºC prior to thermophilic digestion and revealed an increase of 50% in biogas production at 70 ºC with 9h. No effect for high-temperature treatment.

Ferrer *et al.* (2008) studied the effect of a low temperature pretreatment (70 ºC) on the efficiency of the thermophilic anaerobic digestion of primary and secondary waste sludge. The 70 ºC pretreatment showed an initial solubilization effect (increasing volatile dissolved solids by almost 10 times after 9h), followed by a progressive generation of volatile fatty acids. Biogas production increased up to 30% than that of raw sludge.

Evidently, the thermal pretreatment requires the input of a considerably amount of heat, since the sludge feedstock needs to be preheated to the operating temperature (~700kJ/m^3) at the expense of using some of the biogas produced. Moreover, the biogas production is not in proportion to the temperature. Most works have shown that excessively high temperatures (higher than 170-190ºC) lead to decreased sludge biodegradability in spite of achieving high solubilization efficiencies. Indeed, in some cases, there is formation of toxic, refractory compounds during pretreatment which is a major drawback (Delgenes *et al.*, 2002). In previous works, the effect of thermal treatment on biogas production is summarized in Table 3.

Some industrial process based on thermal pretreatment such as Cambi and BioThelys™ have been commercialized. Both processes consist of a treatment at 150-180 ºC during 30-60 min, by vapour injection. The Norwegian company Cambi reports that approximately 30% solids solubilization associated 150% increased of biogas production can be achieved at 180 ºC for 30 min treatment time. BioThelys™ (Veolia Water) thermal hydrolysis process is also a proven and reliable technology leading to increased biogas production, and stabilized biosolids product with increased cake dewaterability.

Chemical pre-treatment

Chemical pretreatment is also an efficient and cost-effective method to hydrolyze the cell wall and membrane and thus increase solubility of the organic matter contained within the cells. According to different principles, chemical methods can be divided to acid and alkaline (thermal) hydrolysis, oxidation. The most frequent studies oxidative methods are ozonation and peroxidation. Acid and alkaline hydrolysis will be introduced in the thermo-chemical pretreatment part.

***Table 4 The effect of ozonation pretreatment on biogas production*.**

Sludge	Treatment conditions	AD conditions	Results
Mixed sludge (Paul et al., 2005)	0.1 g O3.g-1 COD	Batch 30 days 33 ºC	Increase of CH4 biogas production (+100%), respectively
Activated sludge (Bougrier et al., 2007)	0.15 g O3.g-1 TS	Batch 18 days 35 ºC	Increase of biogas production (+145%)
Activated sludge (Valo et al., 2004)	H2O2: 150 mmol.L-1 FeSO4: 5 mmol.L-1 90 ºC, 60 min	Batch 24 days 35 ºC	Increase of biogas production (+16%)

Ozonation

Ozone is a strong cell-lytic agent, which can kill the microorganisms in activated sludge and further oxidize the organic substances released from the cells (Cui & Jahng, 2004; Saktaywin *et al.*, 2005). Of the techniques to disintegrate sludge, ozonation of sludge is one of the effective ways and yields the highest degree of disintegration (Muller, 2000). Following ozonation, the characteristics of the sludge are greatly changes. The flocs are broken down into fine, dispersed particles. Floc integration and solubilization generates a large number of micro-particles dispersed in the supernatant in addition to soluble organic substances (Libing *et al.*, 2009). The sludge biodegradation is affected by ozone dose. Several researchers have investigated the impact of ozone dose on sludge biodegradation. Ozonation treatment has two counteracting effects: degradation of molecules and cell

structures that are undegradable for methanogenic bacteria will increase biogas production; oxidation of organic molecules that are degradable for methanogenic bacteria will decrease biogas production (Levlin, 2010). Saktaywin *et al.* (2005) found that around 60% of soluble COD generated due to ozonation was biodegradable at the early stage of ozonation, while the remaining soluble organic matter was refractory. Yeom *et al.* (2002) showed that when the ozone dose was 0.1 g O_3/g TSS, the biodegradation was about 2-3 times greater compared with raw sludge in both aerobic and anaerobic conditions for 5 days. According to Weemaes *et al.* (2000) the biogas production increased with 80% at ozone treatment with 0.1 g O_3/g COD, the effect was not pronounced at higher ozone concentration. The previous works are summarized in Table 4.

Due to its well-known potential and performance, sludge ozonation is used in combination with activated sludge process in wastewater treatment plant. A review of studies concerning the combination of ozonation with activated sludge process has been recently proposed by Chu *et al.* (2009). The schematic process is as shown in Fig. 2. Ozonation can be introduced to the returned activated sludge line (Route I) or to the sludge digestion line (Route II). For Route I, the ozonation aims to reduce excess sludge production by promoting cryptic growth. As a result, the amount of sludge that can serve as substrate for biogas production is decreased dramatically. However, this combination is beyond the scope of the present paper, the reader who is interested in the principle is referred to the literature of Chu *et al.* (2009). For Route II, ozonation adopted as pretreatment before anaerobic/aerobic digestion is used to enhance the solubility of sludge solids and increase the degree of degradation. Both the final amount of sludge for disposal and the digestion time can thus be reduced. Particularly, for anaerobic digestion, the biogas production can be increased. This process has been commercialized by the Japanese Kurita company and about 30 installations have been implemented (Paul *et al.*, 2005).

Peroxidation

Several peroxidation techniques, including the well-known Fenton peroxidation and novel reactions involving peroxymonosulphate (POMS) and dimethyldioxirane (DMDO), can also achieve a transformation of refractory COD into readily available and soluble BOD, further enhance the biogas production. Fenton pretreatment disintegrates extracellular polymeric substances and breaks cell walls, thus intracellular water is released. Hence the amount of soluble COD and BOD in the sludge water increases considerably. The oxidation process utilizes activation of H_2O_2 by iron salts (F_e^{2+}). A major drawback of this method is the necessity of bringing the sludge to a very low PH. For the full working mechanism of the Fenton peroxidation reaction, the reader is referred to Neyens and Baeyens (2003). More recent research uses alternative peroxidants such as POMS and DMDO which do not require stringent reaction conditions and significantly increase the biogas production during the anaerobic treatment of raw secondary sludge (Dewil *et al.*, 2007).

Raf Dewil *et al.* (2007) studied biogas production when treating sludge with Fenton peroxidation, POMS and DMDO techniques prior to anaerobic digestion on lab-scale. The results showed a maximum increase of 75% was measured with Fenton, while the POMS treatment increased the biogas production by a factor of nearly 2, against an even higher 2.5 for the DMDO treatment.

Other oxidant

Recently, a new oxidant peracetic acid (PAA) has been proposed to enhance anaerobic digestion biogas production. PAA has a strong effect of oxidation on microorganism. It's reported that PAA is able to destroy the barrier of spores, dissolve the core, and make the material such as DNA protein leaking. It can be inferred that PAA can dissolve and oxidize cells to promote the release of organic matter, thereby reduce the sludge volume and improve the efficiency of subsequent anaerobic digestion (Shang & Hou, 2009). For the principle of the oxidation process, the reader is referred to Shang et al. (Shang & Hou, 2009). According to their experiments, the excess sludge was pretreated by PAA, and then anaerobic digestion was conducted for 20 days in 35 ºC to detect the biogas production compared with the sludge without pretreatment. The results showed that the total biogas production was enhanced 72% than that of the raw sludge. They also observed that at the PAA concentration of 0.011%, there was almost no PAA or H_2O_2 left in excess sludge solution after 12 hour's reaction. Hence it avoids the harmful caused by the sterilization of PAA to the anaerobic microorganism. This method has to be further studied in order to take into practice on a large scale in future.

Wet oxidation method has also been applied in sludge treatment. This process uses oxygen or air at high temperature (260 ºC) and pressure (10MPa) (Zimpro Environmental, 1993). The method can solubilize a large part of the sludge but the problems with odour, corrosion and high energy cost restrict its practical applications.

Thermochemical pre-treatment

Alkali treatment is normally combined with thermal treatment; it's so called thermochemical treatment. There is no consensus on the efficiency of alkali agents. J. Kim *et al.* (2003) showed that the order of efficacy in sludge solubilization was

$NaOH>KOH>Mg(OH)_2$ and $Ca(OH)_2$, whereas Penaud *et al.* (1999) demonstrated that pretreatment with KOH was more efficient than using NaOH. With regard to the effect of thermochemical pretreatment (addition of alkali) on solubilization and biodegradability, different studies give contradictory results. Indeed, Haug *et al.* (1978) determined a decrease in biodegradability of 60%, while Penaud *et al.* (2000) observed no effect on the biodegradability. Tanaka *et al.* (1997) showed that thermochemical pretreatment led to significant increase in biodegradability, which could reach 230%. It's noted that thermochemical pretreatment gives the best results in the biogas production compared with thermal, chemical, ultrasonic methods under the same conditions. Kim *et al.* (2003) compared the four pretreatment methods, they selected optimum conditions for thermal (121 ºC for 30 min), chemical (7 g/l NaOH addition), ultrasonic (42 kHz for 120 min) and thermochemical (121 ºC for 30 min, 7 g/l NaOH addition) pretreatments, in the end, they got the biogas production following the anaerobic digestion of the thermally (4842 l/m^3 WAS), chemically (4147 l/m^3 WAS), ultrasonically (4413 l/m3 WAS) and thermochemically (5037 l/m^3 WAS), respectively. Valo *et al.* (2004) tested the COD removal rates and biogas production under two conditions (thermal treatment at 170 ºC and thermo-chemical at 130 ºC with PH = 10 for 30 min, continuous anaerobic digestion). They found that the COD removal rates were significantly increased compared with the untreated raw WAS, being 71% and 60% of raw WAS COD, for thermal and thermochemical treatment respectively, while the biogas productions were increased by 54% and 74%.

Table 5 The effect of thermochemical pretreatment on CH4 production

Sludge	Treatment conditions	AD conditions	Results
Activated sludge (43 g.L-1) (Stuckey & McCarty, 1978)	300 meg NaOH. L-1 175ºC 60 min	Batch 25 days 35 ºC	Increase of CH4 Production (+62%)
Activated sludge (industrial, 8.4 g.L-1) (Tanaka et al., 1997)	0.3 g NaOH. g-1 VSS 130 ºC 5 min	Batch 10 days 37 ºC	Increase of CH4 Production (+31%)
Activated sludge (17 g.L-1) (Kim et al., 2003)	7 g NaOH. L-1 121 ºC 30 min	Batch 7 days 37 ºC	Increase of CH4 Production (+38%)
Activated sludge (30 g.L-1) (Heo et al., 2003)	45 meg NaOH. L-1 55 ºC 240 min	Batch 20 days 35 ºC	Increase of CH4 Production (+88%)
Activated sludge (17 g.L-1) (Valo et al., 2004)	1.65 g KOH. L-1 pH: 10 130 ºC 60 min	CSTR 25 days 35 ºC	Increase of CH4 Production (+75%)
Activated sludge (Dogan & Sanin, 2009)	Microwave: 160 ºC pH: 12 by NaOH 16 min	Semi-continuous 15 days 37 ºC	Increase of CH4 Production (+53%)

Other thermochemical experiments have been studied with hydrogen peroxide and Fenton's reagent (Valo *et al.*, 2004), but the result showed no evident improvement in COD solubilization and the biogas production was lower than the level obtained after the thermal treatment at 130 ºC.

Performance improvements in methane production are summarized in Table 5.

Mechanical pre-treatment

Mechanical pretreatment plays an important role because it favors solubilization of particulate matters in liquid phase. In general, the most often used techniques in mechanical pretreatment are ultrasonication, grinding and high pressure homogenization. By these methods, the aim is to increase the degradability of organic matters by disrupting the flocs and/or lysing the bacterial cells. The principles and applications of the methods above will be introduced hereafter.

Ultrasonic pre-treatment

Ultrasonication is a promising and effective mechanical pretreatment method to enhance the biodegradability of the sludge. This technology has several inherent merits like efficient sludge disintegration (>95%), improvement in biodegradability, improved biosolids quality, increase in methane percentage in biogas, no chemical addition, less retention time, sludge reduction and energy recovery (1kW) of ultrasound energy generates 7 kW of electrical energy including losses (Pilli *et al.*, 2010). Ultrasonication enhances the sludge digestibility by disrupting the physical, chemical and biological properties of the sludge. As mentioned above, hydrolysis is the rate-limiting step in anaerobic digestion process. Ultrasonic lysis accelerates the hydrolysis reactions by disrupting cells. The bacterial cells are disunited by pressure waves and cavitation generated from an ultrasonic generator leading to elution of intracellular organic substances (Takatani *et al.*, 1981). In addition, some soluble particulate organic matter may even be transformed into a soluble state under the cavitational explosion of transient bubbles. The disruption of sludge particles derived from sonication treatment would enhance subsequent acidogenesis, acetogenesis and methanogenesis reactions, which would in turn lead to an improvement in methane generation and reduction of sludge volume (Kuan *et al.*, 2007).

There are two key mechanisms associated with ultrasonic treatment: cavitation, which is favored at low frequencies, and chemical reactions due to the formation of OH-, HO_2, H^+ radicals at high frequencies (Carr`ere *et al.*, 2010). High-power ultrasound (200W) is generally performed at low frequencies (20 kHz) in order to get an effective sludge disruption. The mechanical phenomena of sludge sonication leads to sludge floc disintegration and microorganisms' lyses, according to the treatment time and power, equating to specific energy applied (Chu et al., 2002). The effect of sonication time on the sludge disintegration and the subsequent anaerobic digestion (batch test) was evaluated by Wang *et al.* (1999). They tested the methane amount under different sonication time groups when other parameters were the same (9 kHz, 200 W, and 20-25 ºC). The results showed that, compared with the control, the methane amount increased by 12%, 31%, 64% and 69% on the

11th day, with corresponding ultrasonic pretreatment of 10 min, 20 min, 30 min and 40 min, respectively. The optimum pretreatment for enhancing the methane generation should be approximately 30 min. Although cell disintegrations of 100% can be obtained at high power levels, power consumption then becomes a serious drawback (Weemaes & Verstraete, 1998). Rana Kidak *et al.* (2009) showed that the efficiency of the sludge disintegration was higher with higher power, but if considered the particle size, there was no further decrease of the particles when the ultrasonic power was beyond 100 W. They also summarized the conclusion that high power-short retention time was more effective than low power-long retention time for municipal sludge. Considering energy consumption and enhancement of anaerobic digestion performance, applied specific energies are usually in the range from 1,000 to 16,000 kJ.kg^{-1} TS although biogas production increases with the energy input (Salsabil *et al.*, 2009). Bougrier *et al.* (2005) tested the optimum specific energy of ultrasound treatment on biogas production. According to their results, biogas production increased with energy supplied when ultrasonic specific energy between 0 and 7000 kJ/kg TS. But for energy supplied of 7000 and 15,000 kJ/kg TS, biogas production was almost the same. The optimum ultrasonic energy was thus about 7000 kJ/kg TS.

Table 6 The effect of ultrasonic pretreatment on biogas production

Sludge	Treatment conditions	AD conditions	Results
Activated sludge (TS 3.5%) (Anders, 2005)	8.4 kWh/m3 400 W 6 min	Semi-continues Lab-scale	Increase of gas production (+13%)
Mixed sludge (Bien et al., 2004)	20 kHz 180 W 60 s	Batch 28 days 35 ºC	Increase of biogas production (+24%)
Activated sludge (27 g TS L-1) (Bougrier et al., 2005)	20 kHz 7,000 and 15,000 kJ.kg-1TS	Batch 16 days 35-37 ºC	Increase of biogas production (+40%)
Activated sludge (Braguglia et al., 2008)	5,000 kJ.kg-1TS	Semi-continues HRT: 20 days	Increase of biogas production (+36%)
Activated sludge (17.1 g TS L-1) (Salsabil et al., 2009)	20 kHz 108,000 kJ.kg-1TS	Batch 50 days 37 ºC	Increase of biogas production (+84%)
Activated sludge (2.14% TS) (Erden & Filibeli, 2009)	20 kHz 9690 kJ.kg-1TS	Batch 35 days 36 ºC	Increase of biogas production (+44%)
Activated sludge (Perez-Elvira et al., 2009)	30 kWh.m-3 sludge	Batch	Increase of biogas production (+42%)
	30 kWh.m-3 sludge	Continuous HRT: 20 days	Increase of biogas production (+37%)

The primary aim of ultrasonication is to increase the sludge biodegradability to enhance the biogas production at lower HRT in anaerobic digester. Tiehm *et al.* (1997) conducted batch experiments at different HRTs of 22 days, 26 days, 12 days and 8 days. Compared to the untreated sample with 22 days, ultrasonication of sludge was observed to enhance volatile solids reduction and biogas production in anaerobic digestion. The results showed that the biogas production for the disintegrated sludge at 22 days residence time was 36.36 L/day and at 8 days, the biogas production was 100 L/day with the volatile solids reduction of 50.3% and for the control the volatile reduction was only 45.8% at 8 days retention time.

Previous work done on ultrasonic pretreatment of sludge is summarized in Table 6.

Ultrasounds served as pretreatment for anaerobic digestion have been implemented extensively in industry. The German company Hielscher is professional in ultrasound technology. Since 1999, Hielscher has been supplying ultrasonic disintegration systems of up to 48kW individual power to various waste water treatment plants as well as to municipal and industrial waste treatment facilities all around the world. Some of these systems improved the biogas yield by up to 25% (Hielscher, 2010).

Grinding

One predominant technique is the wet milling, which is more of a grinding method. Wet milling uses small beads to rupture cell walls, the size of the beads used are thus critical for maximal sludge disintegration (Baier & Schmidheiny, 1997). Of several milling devices, the ball mill using small diameter (0.2-0.25 mm) balls has the best performance (Allan & Talat, 2007). The use on an agitator ball mill was studied by Kunz *et al.* (1994). Sludge was pressed through a cylindrical or conical space by an agitator including shear-stresses high enough to break the bacterial cell walls. The impact on methane production is shown in Table 7.

Table 7 The effect on biogas production of grinding and high pressure homogenizer methods.

Sludge	Treatment conditions	AD conditions	Results
Activated sludge (SRT: 7 days) (Baier & Schmidheiny, 1997)	Balls diameter: 0.25 mm Balls velocity: 10 m.s-1 9 min, 60 ºC	Batch 21 days 37 ºC	Increase of biogas production (+10%)
Anaerobic digested Sludge (Baier & Schmidheiny, 1997)	Balls diameter: 0.25 mm Balls velocity: 10 m.s-1 9 min, 60 ºC	Batch 21 days 37 ºC	Increase of biogas production (+62%)
Activated sludge (Choi et al., 1997)	Plate collision ∆P: 30 bar	Batch 26 days 35 ºC	Increase of VS removal (+43%)
Activated sludge (Engelhart et al., 1999)	Homogenizer ∆P: 300 bar (750 kJ.kg-1 TS)	CSTR HRT: 10-15 days 35 ºC	Increase of CH4 production (+60%)
	Homogenizer ∆P: 600 bar	CSTR HRT: 20 days 36 ºC	Increase of biogas production (+18%)

High pressure homogenizer

One of the most frequently used methods for large-scale operation is high pressure homogenization, compressing the sludge to 60 MPa (Harrison, 1991). The compressed suspension is then depressurized through a valve and projected at high speed against an impaction ring. The cells are hereby subjected to turbulence, cavitation and shear stresses, resulting in cell disintegration (Lise *et al.*, 2008). Some studies reporting the effects of high pressure homogenizer on biogas production are also summarized in Table 7.

Lacking of available literatures on mechanical pretreatment, the methods mentioned above are not comprehensive. However, it's seen that their efficiency of improving anaerobic digestion of waste activated sludge is rather lower than other methods.

Other pretreatment methods

The use of microbial enzymes for the enhancement of degradation of waste activated sludge called the Enzymic Hydrolysis (EH) process was proposed by Mayhew *et al.* (2002). EH process was first used to kill pathogens, however, an enhancement of biogas production was observed during anaerobic digestion. Hereby, the method aroused interest of researchers. Mayhew *et al.* (2003) kept the WAS at 42 ºC using a holding chamber, with 2 days' retention time of EH stage in lab scale, they found a 10% improvement in biogas production. Miah *et al.* (2004) measured a 210% enhanced biogas production during thermophilic digestion (at 65 ºC) caused by the protease activity of the Geobacillus sp. Strain AT1.

Table 8 Estimated costs, merits and demerits

Method	% cell disintegration	Estimated cost (EURO per tonne TDS)	Major merit	Major demerit
Thermal (Cambi)	30	190		Relatively low yield,dependence on sludge type
Oxidation (German Bayer-RLoprox)	90	800	High disintegration efficiency	Low pH, corrosive, high cost
Thermochemical	15-60	Not available	Relatively simple	Corrosion, odour
Ball mill	90	414-2500	High efficiency Relatively simple	Energy intensive
High pressure homogenization	85	42-146	High efficiency Low energy levels	Complicated
Ultrasound	100	8330	Complete disintegration	Energy intensive
Thermochemical	15-60	Not available	Relatively simple	Corrosion, odour Subsequent neutralization

Microwave pretreatment is another method which has already been proven to enhance anaerobic digestion. In a lab study by Park *et al.* (2004), an oscillation frequency of 0.3-300 GHz was used during a 15 min exposure of sludge containing 1.9% VS. The results showed the total COD removal and methane production increased 64% and 79%, respectively, compared with a conventionally operated mesophilic digester.

The anoxic gas flotation (AGF) process as an innovative anaerobic digestion process also has the potential to enhance biogas production. This process uses anoxic gas to float, concentrate and return bacteria, organic acids, protein, enzymes and undigested substrate to the anaerobic digester for the rapid and complete conversion of waste sludge to gas and soluble constituents (Dennis, 2000). By virtue of greater solids destruction and gas scrubbing of AGF process, methane production can be enhanced and also the biogas quality can be improved. In 1998 a full-scale AGF plant was installed at the SWSSD treatment plant in Burien, WA, USA. The AGF process increased the biogas methane concentration from 64% at the digester to 80% as a final product. At the same time, the AGF facility achieves a 72% volatile solids conversion to gas at a loading of 3.15 Kg/m3/d (Jesús *et al.*, 2006)..

The thermal-oxidative treatment to enhance biogas production was evaluated by *Jesus et al.* (2006). A group of experiments were made, including thermal, oxidative as well as thermal-oxidative separately with different locations. The results showed that when the recycled sludge was thermo-oxidized with 2gH_2O_2/g $VSS_{influent}$ at 90 ºC before being returned to the anaerobic digestion reactor, the biogas production achieved the largest amount compared with thermal or oxidative and conventional methods.

COMPARISON OF PRETREATMENT METHODS

Although these pretreatment methods contribute to accelerating anaerobic digestion and enhancement of biogas production, they have their own drawbacks. Thermal pretreatment requires of a considerable amount of heat to preheat the sludge feedstock, so it's unavoidable to consume some of biogas produced. Ultrasonication is no doubt the most powerful method to disrupt cell walls, but power consumption becomes a serious drawback (Weemaes & Verstraete, 1998). Other mechanical methods such as grinding and high pressure homogenization are less effective than other methods. Even ball milling are not always impactful. Baier *et al.* (1997) found several industrial sludges failed to be affected by this technique. Although they do not require chemicals or heat, most of mechanical techniques consume a lot of power. Regarding oxidative methods, both the cost and energy consumption of ozone production are high. While peroxidation method is likely to bringing the sludge to a very low pH (optimum at 3), which inhibits methanogenic bacteria's activity. Thus the cost of chemical reagent to adjust the pH has to be taken into account. In addition, according to the study of Weemaes *et al.* (1998), the most important sludge pretreatment methods are summarized together with their costs, advantages and drawbacks (Table 8).

Due to the characteristics of sludge (primary, waste activated, digested, sludge age…) and the anaerobic conditions (batch, continuous, HRT, temperature…) as well as the practical application (pilot-scale, full-scale…), it's difficult to compare the effect of pretreatment methods described above. However, the present paper focuses on waste activated sludge from municipal wastewater treatment plants and biogas production. A few literatures provide valuable comparative analysis of the pretreatment methods under the same conditions.

As underlined in the 3.4 section, Kim *et al.* (2003) selected optimum conditions for thermal, chemical, ultrasonic and thermochemical pretreatments, in the end, they got the order according to biogas production: thermochemically > thermally > ultrasonically > chemically.

Bougrier *et al.* (2006) compared the effect of ultrasound, thermal hydrolysis and ozonation pretreatment on the same activated sludge sample prior to batch mesophilic anaerobic digestion. All three pretreatments improved biogas production. For ozonation (0.10 and 0.16 g O_3 g^{-1} TS), this enhancement was low (246–272 mL CH4 g^{-1} CODin against 221 mL CH_4 g^{-1} COD in for the raw sludge) compared to sonication (with a specific energy of 6250 and 9350 kJ kg^{-1} TS) and thermal hydrolysis (at 170 or 190 ºC), which both resulted in the same outcomes (325–334 mL CH4 g^{-1} CODin).

Barjenbruch *et al.* (2003) compared thermal treatment (80–121 ºC), high pressure homogenization (600 bar) and enzymatic treatment (carbohydrase addition) for pretreatment prior to continuous anaerobic digestion with 10 days HRT. An increase of biogas production was observed in the following order: low intensity thermal treatment at 90 and 121 ºC (>20% increase) > high pressure and thermal treatment at 80 ºC (>16–17% increase) > enzymatic treatment (>13% increase).

Strictly speaking, it is not comprehensive to compare these methods only in term of biogas production. Also in practice, the solubilization of sludge, dewaterability, total suspended solids and energy cost as well as chemical consumption have to be taken into account. In view of limited literature, the emphasis has just been laid on the biogas production of the pretreatment methods.

CONCLUSION

There are currently considerable concerns in developing efficient and environmental friendly ways to convert waste activated sludge to biogas, as clean, renewable fuel for multiple utilizations. It is well known that the hydrolysis is the bottleneck in anaerobic digestion. The predominant techniques used to overcome the problem are reviewed in this paper.

As shown in Table 8, it is hard to say which method is the best because each has its own strongpoint and weak point. Yet, until now, none of the pretreatment technologies has found a real breakthrough. Mechanical pretreatment methods often appear to require high capital equipment and are energy intensive. Thermal and thermochemical methods usually require high temperatures to achieve acceptable results. Oxidative methods cost high and have the problem of low pH. However, until recently, it appears that taking into account the increased costs of sludge disposal, the operational cost and the investment needed for sludge ozonation may be offset by the decreased operational costs for sludge treatment and disposal. Hence, sludge ozonation may become a cost-effective opportunity.

In order to obtain the biogas production as high as possible, as well as to reduce the excess sludge disposal, considerable efforts are needed in further research in the future.

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