Anaerobic Digestion
STATE OF THE ART OF ANAEROBIC DIGESTION OF MUNICIPAL SOLID WASTE IN EUROPE

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ABSTRACT To consider anaerobic digestion as a hype or a passing trend would dishonor the technology and its entry in the household waste treatment industry and moreover, it would be wrong. Since the introduction of anaerobic digestion of MSW and biowaste in the beginning of the nineties, the adoption of the technology has consistently grown. Considering that twenty years ago only a handful of digesters were running on biowaste or municipal solid waste and that now almost 200 plants will be up and running in Europe by the end of 2010, one can not dispute that AD is a mature technology. And the number of countries in Europe that tend to stimulate the treatment or pre-treatment of their household waste via anaerobic digestion continues to grow. An inventory of the existing, contracted plants and plants under construction was made in order to get a good overview of the state of the art of the technology in 2010. Due to the extended analysis-period (1990-2011), some clear trends can be observed.

The installed capacity of anaerobic digestion is indisputably on the rise. Where a mere 15 plants were installed by the end of 1995 (with an installed capacity of about 220,000 tons), and more than 70 plants treating biowaste or MSW were installed during the last five years in Europe. The expected installed capacity by the end of 2010 will be about 6,000,000 tons per year divided over 200 plants in 17 countries.

Although the fundamental anaerobic digestion process is more or less the same in all the plants, the technology can be classified into different categories according to operating parameters. Market data and case studies of some state-of-the-art plants will be presented as examples.

Keywords: Anaerobic digestion, Municipal solid waste, Biogas
PERFORMANCE OF A COMMERCIAL-SCALE DICOM™ DEMONSTRATION FACILITY TREATING MIXED MUNICIPAL SOLID WASTE

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ABSTRACT Mixed domestic municipal solid waste (MSW) collected during a 5 day period (320t) was delivered to a commercial-scale (20,000tpa) DiCOM™ demonstration plant in Perth, Western Australia and mechanically sorted into reject (49%) and organic (OFMSW) (51%: containing 11% inert material; C:N = 33:1; moisture = 56%; VS = 80%) streams. The captured OFMSW was loaded into the bioconversion vessel which was maintained under aerobic conditions during loading. Once loaded, the reactor was sealed and flooded with an anaerobic inoculum to initiate the high solids (30% dry matter (DM)), thermophilic (55°C) anaerobic digestion (AD). Methane (CH₄) was produced within 3 hours. The substantial inoculum enabled a stable and highly productive AD without the need to adjust pH. From the biogas generated (160m³ CH₄/dry t OFMSW), the theoretical electrical and heat (0.65MWh and 2.6GJ per dry t OFMSW) yield of the biogas at full commercial operation was estimated and found to be in excess of that required for plant operation (0.22MWh and 0.30GJ per dry t OFMSW). The anaerobic liquor was drained after 11 days of AD and the drained solids retained in the reactor and aerated to provide a rapid 1 week in-vessel composting. After a total treatment of 21 days the digested and composted solids were unloaded as composted soil conditioner.

Keywords: Solid Waste, Anaerobic digestion, Composting, Hybrid, Thermophilic

Introduction

Increases in world population density and associated waste production, coupled with dwindling available land, increased fuel/transport costs and the need for environmentally sustainable waste treatment, has highlighted the need for close-to-source waste treatment facilities with small footprint. The DiCOM™ process is a natural biological system for the treatment of municipal solid waste (MSW) combining high solids (20-40% DM), thermophilic (55°C) anaerobic digestion (AD) with in-vessel composting within a single vessel. The twenty one (21) day batch process allows for sequential aerobic-anaerobic-aerobic treatment of the mechanically separated OFMSW within a single, completely sealed vessel, the end-products being a compost and renewable energy in the form of biogas. After successful operation at laboratory and pilot-scale, a commercial-scale DiCOM™ demonstration facility (20,000tpa) was constructed at the site of the Western Metropolitan Regional Council (WMRC) Waste Transfer Station (WTS) in Perth, W.A. The plant, which consisted of a proprietary mechanical sorting system (rotating trommel), conveying arrangements and a single DiCOM™ bioconversion vessel, was commissioned in February 2009. This paper outlines the performance of one of a series of commissioning trials, operated to test energy efficiency, biological process stability and end-product quality.

Materials and Methods

During normal WMRC waste collection operation (6 to 10 July 2009), all mixed domestic MSW collected (320t) was introduced (~15t/h) into the DiCOM™ mechanical sorting system (Fig. 1). Bore water (~28L/min) was introduced to the trommel to reduce dust and improve organic separation efficiency. Oversized objects generated a reject stream that was directed to landfill. All domestic MSW received was processed on a daily basis, with the captured organic fraction (OFMSW) transported, by the conveying system into the DiCOM™ bioconversion vessel.
Ambient air drawn into the reactor during loading ensured the reactor headspace remained aerobic. At the conclusion of daily waste processing, and during post-anaerobic treatment, the reactor was sealed and the contents exposed to an aeration regime designed to avoid channelling of air as follows: Pressurised air was introduced into the vessel to raise the internal pressure to a predetermined set-point at which time the air flow was stopped. The over-pressure was maintained for a “soak” period prior to being released (Fig. 2). This aeration cycle was repeated continuously during post-anaerobic treatment and overnight during loading with odorous air treated via acid scrubbing and activated carbon to remove odour. The frequency of the cycling could be managed automatically by DCS feedback control.

At the conclusion of loading, the reactor was sealed and the headspace flushed with an inert gas to create an oxygen-free atmosphere. The OFMSW (C:N of 33:1; moisture content of 56%; VS content of 80%; 8% protein; 4% lipids; 32% cellulose; 7% hemicellulose; 12% lignin) contained within the reactor was fully submerged with an anaerobic liquor/inoculum (320 m³) from a previous DiCOM™ trial. The liquor was recirculated via a heat exchanger to maintain the temperature (55±3°C) and improve process monitoring and
control. Biogas generated was characterised (Advanced Optima Continuous Gas Analyzer AO2040) and quantified (ST98 FlexMASSter™ mass flow meter) before being flared. After 11 days of anaerobic digestion (day 16: Fig. 2), the anaerobic liquor was drained and stored anaerobically for use as inoculum in subsequent trials. The solids were dewatered anaerobically (55% moisture) prior to the vessel headspace being transitioned from being methane (CH₄) rich (65%) to aerobic using an inert gas and air. At this time, cyclic air pressurisation was again initiated. The composted end-product was removed after 21 days of DiCOM™ processing.

The plant was monitored and operated by a dedicated, purposed built, computer distributed control system (DCS) via a process field bus (PROFIBUS) interface. pH, redox, liquor and solids temperature, hydrostatic, air and biogas pressure, gas and liquid flow rates, motor current draw, electricity consumption, liquid and solid fill levels, O₂, CH₄ and CO₂ concentrations were computer monitored, logged and used as control parameters.

Liquid samples collected for analysis (NH₄⁺, volatile fatty acid (VFA) were centrifuged immediately (14,000rpm for 10min) and the supernatant stored (-20°C). The moisture and volatile solids content of solid samples and NH₄⁺ concentration in liquor samples were determined according to standard methods [1]. VFA were analysed as described previously [3]. The grit/heavy (inert) fraction was separated by agitating MSW in water (solid: liquid = 1:10 w/v) and decanting the suspended slurry through a 1mm square mesh. MSW characteristics were analysed by ChemCentre, Bentley, W.A. Process water analysis was performed by ALS Water Resource Group, Malaga, W.A. Compost samples were analysed for compliance with the Australian Standard for Composts, Soil Conditioners and Mulches (AS4454–2003) [2] by RichGro Pty Ltd, Jandakot, W.A.

Results and Discussion

For the described trial approximately 200t (Fig. 3) of material was introduced into the bioconversion vessel. During the three week processing period, the DiCOM™ process provided a 35% reduction in OFMSW mass (40% VS destruction) (Fig. 3), with the solids being converted into gaseous end-products (biogas) by microbial metabolism. The water generated from this biological degradation of the organics, and that added to improve organic separation efficiency (37t), was found to accumulate within the system (Fig. 3). Consequently, continued operation of the system under this operational regime (i.e. fresh water being added to trommels), will require discharge of liquor from the process. The production of wastewater could however be minimised by using process water to improve organic separation efficiency. The inert material in the final product (37t) is due to the fact that glass and grit removal technology was not yet implemented in this trial.

Figure 3. Mass balance for a commercial-scale DiCOM™ batch trial

The anaerobic digestion phase of the DiCOM™ process was found to be stable (Fig. 4). Even though VFA accumulated during the initial days of anaerobic digestion (350mM: Fig. 4), the buffer capacity of the anaerobic liquid was adequate to avoid acidification (pH: 6.8–7.8) without requiring process control intervention. Rapid acetate removal (7.5mM/h) coincided with the maximum CH₄ production rate (Fig. 4: 1.2m³/h/t dry OFMSW/h = 1.5m³/h/t VS) and indicated that significant acetoclastic methanogens were present within the reactor after 3 days of anaerobic treatment. This observation, also noted during laboratory and pilot-scale trials, suggests that the reuse of liquor is an effective method to transfer a viable
methanogenic culture. Acetate and butyrate were degraded within the reactor while propionate accumulated, but was readily degraded during anaerobic, thermophilic liquor storage between trials (data not shown).

CH₄ production (160 m³/dry t OFMSW = 0.22 m³/kg VS) in this study is comparable to literature values for thermophilic AD of OFMSW (Table 1). Using an electrical and heat conversion efficiency of 39.7% and 74%, respectively, the energy output from the CH₄ generated was 0.65 MWh and 2.6 GJ per dry t OFMSW. Considering operation of a commercial-scale facility (55,000 tpa), consisting of 3 DiCOM™ bioconversion vessels each processing 700t of OFMSW (55% moisture), the energy production and consumption of the facility can be estimated. An extrapolation based on data from the current trial, estimated that the electrical and heat requirements for operation (0.22 MWh and 0.30 GJ per dry t OFMSW) are less than the energy yield of the biogas that would be produced (0.65 MWh and 2.6 GJ per dry t OFMSW).

![Figure 4. VFA and pH time course during the anaerobic phase of a DiCOM™ batch trial.](image)

**Table 1. Process parameters and biogas yields of thermophilic (50–56°C) anaerobic digestion of OFMSW [4]**

<table>
<thead>
<tr>
<th>Process</th>
<th>Capacity</th>
<th>Waste</th>
<th>TS During AD (%)</th>
<th>HRT (d)</th>
<th>Biogas Yield (m³/kg VS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DiCOM™a</td>
<td>900 m³</td>
<td>Mechanically-sorted OFMSW</td>
<td>17</td>
<td>12</td>
<td>0.44</td>
</tr>
<tr>
<td>BTA</td>
<td>3.4 m³</td>
<td>Source-sorted (SS) OFMSW</td>
<td>6–16</td>
<td>12</td>
<td>0.39</td>
</tr>
<tr>
<td>DRANCO</td>
<td>56 m³</td>
<td>Organic household waste - no paper</td>
<td>30–35</td>
<td>15–21</td>
<td>0.45</td>
</tr>
<tr>
<td>KOMPOGAS</td>
<td>200 m³</td>
<td>Fruit, yard and vegetable waste</td>
<td>15–40</td>
<td>13</td>
<td>0.39</td>
</tr>
<tr>
<td>SEBAC</td>
<td>3 X 0.7 m³</td>
<td>OFMSW (paper, yard, food waste)</td>
<td>–</td>
<td>21</td>
<td>0.34</td>
</tr>
</tbody>
</table>

* Current study

As not all sorting technologies were installed for this trial (e.g. glass, grit, heavies, film plastics), the solids end-product contained physical and possibly chemical contaminants. Consequently, the solid end-product was tested against AS4454–2003 [2], without reference to chemical and physical contaminants, and was found to be classified as a composted soil conditioner.

**Conclusion**

The successful DiCOM™ demonstration facility trials, as judged by independent auditing engineers (Sinclair Knight Merz and GHD, Perth, W.A.), facilitated expansion of the technology to commercial...
operation (55,000 tpa), with construction currently in progress. The trials have led to design improvements so as to maximise methane output and increase product stability.

References
DEVELOPMENT OF ANAEROBIC COLUMN REACTOR (ACR) FOR BIOMETHANATION OF FOOD WASTE

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ABSTRACT The development of a lab-scale anaerobic column reactor (ACR) was carried out for efficient biomethanation of high concentration food waste slurry (FWS) at minimum acceptable hydraulic retention time (HRT) of 3d. The experiments were performed with a FWS of different concentrations ranging from 5% to 50% at various HRTs ranging from 28d to 3d in batch and semi-continuous mode. The methane production was 0.5 m³/kg TVS added. The digested sludge, due to its nutrient and humus contents, was useful as a soil conditioner. Semi-continuous mode of operation was more efficient than batch process for biomethanation of FWS with 20% concentration at 3d HRT.

Keywords: Biomethanation, Food waste, Column reactor, Biogas

Introduction
The FW is a significantly large fraction of the MSW (20-65%) [1], which increases as per the class of the society. Food waste (FW) constitutes approximately 15-45% of the total municipal solid waste (MSW) in India. The minimum (15%) being from individual dwellings and the maximum (45%) from the eateries and marriage halls. In India, the FW, at present is carried away along with the MSW and disposed off by using the methods such as landfill, incineration, composting, and sometimes recycled as animal feed. Incineration is expensive whereas other methods cause secondary environmental pollution, besides exploiting costly land. Complete decomposition of total volatile solids (TVS) in FW is a feasible method for which a high-rate aerobic slurry bioreactor with continuous agitation was recommended [2]. The energy and mechanical devices required for oxygenation and agitation of FW increases the treatment cost while producing excess sludge as compared to biomethanation process.

The biomethanation potential depends on the composition of the FW i.e. relative contents of proteins, lipids, carbohydrates and cellulose. The food wastes, irrespective of its source are not homogeneous and diurnal variations are observed in the composition, which makes the biomethanation of FW even more challenging. Hence, a development of ACR and its performance was evaluated for 200 days for its practical applicability for recovery of methane during anaerobic biomethanation of the food waste slurry (FWS).

Furthermore, the bioenergy, and the bio-sludge obtained from the process would compensate to some degree the cost of treatment. In-depth parametric studies are lacking in the literature[3] hence the paper evaluated the effect of operational and other parameters such as loading rate, VFA concentration, HRT, etc.

Anaerobic Column Reactor (ACR)
The vertical column reactor was fabricated from PVC material and installed in the laboratory. The net volume of the ACR was 25 L excluding space for biogas collection consisted of a vent at the top, sludge disposal point at the bottom and sample sludge collection ports at various positions along the height of the ACR. The biogas collection vent was attached to the biogas collection cum measurement assembly.

Reactor Operation
The FWS was fed to the ACR manually from the top and the content of the reactor was recycled continuously to improve mixing conditions by the peristaltic pump (Watson Marlow make). The quantity of FWS fed to the reactor was equal to the quantity of the reactor mixed slurry (MLSS) withdrawn for keeping the working volume constant and to maintain the particular HRT. Samples of the reactor mixed liquor were collected before feeding fresh FWS.
Owing to the alternate gradual contraction and expansion of the reactor portions the pressure drop occurred and the eddies were formed. The pressure drop in the reactor helped in controlling the washout of the suspended particulate matter i.e. substrate and biomass. Furthermore, the eddies formed caused turbulence within the reactor which prevented the settling of the particles and further enhanced the mixing of the reactor content.

**Materials and Methods**

The FW was collected from 6 houses alternatively with average water content 50 ± 9.5%. The dried FW contained 49 ± 3% carbon and 8.3 ± 0.9% nitrogen. The collected FW was mixed thoroughly and shredded with grinder/mixer to particle size of about 0.35 mm. The FWS was prepared by mixing tap water in the wet grinded paste of the FW and then mixed thoroughly. The FW was used in a wet form as slurry for feeding and other analysis purposes and described on a dry weight basis. The samples were centrifuged at 3000 rpm for 15 min and the supernatant was filtered through a 0.45 µm membrane filter (Millipore, USA) for analysis of dissolve organic carbon (DOC). DOC was measured with a TOC analyzer (Shimadzu, Japan). The physico-chemical analysis was performed as per the Standard Methods (APHA, 2005)

**Results and Discussion**

The same lab-scale ACR was operated in both the modes, batch and semi-continuous mode with 100% continuous recirculation of the reactor content from the outlet at the top to sludge outlet provided at the hopper bottom. The food waste has been observed to be a highly suitable substrate for anaerobic digestion with regard to its high biodegradability and methane yield. Macro and micronutrients were observed to be well balanced for anaerobes. Since, the total concentration will not change significantly during anaerobic digestion, the effluent can be essentially used as an organic fertilizer [4]. The C/N ratio of FW was 15.3 and sulfur (S), calcium (Ca) and magnesium (Mg) contents were 0.25%, 20.16% and 0.14% net weight basis respectively.

**Start-up**

For the start-up of ACR, the inoculum was obtained from the anaerobic digester treating secondary sewage sludge. The concentration of suspended solids (SS) and volatile suspended solid (VSS) of the inoculum were 4500 mg/L and 3850 mg/L respectively. ACR start up was carried out by filling the reactor with digested sludge and FWS (5%) in 9:1 ratio, and the contents were thoroughly mixed by recirculation. After 7 days (d), the effluent CODs and methane (CH₄%) content in biogas were 200 mg/L and 68% respectively which indicated that the reactor start-up was over and further loaded with different FWS concentrations such as 10%, 15%, 20%, etc.

**ACR Operation Batch Mode**

The batch-mode operation was carried out at the HRT of 3d. the FWS of 10% concentration (dry wt./vol.) was added and recirculation was continued for 3d. Once the consistent results were obtained the, FWS concentration was increased to 15%, 20%, 25%. The COD reduction of 90% was obtained at FWS concentrations of 15% and 20% which reduced below 80% at 25% FWS concentration. The biogas generation was also found to be hampered at the FWS concentration of 25%.

The deterioration of the performance at higher concentration of FWS might be due to the hampered biomass-substrate mixing thereby limiting the mass transfer. The biogas generation and COD reduction drastically reduced at 1d HRT, whereas they were found to be only marginally improved at higher HRTs than 3d. Hence, HRT of 3d was considered as an optimum HRT. The literature review indicated that almost all the studies on biomethanation of FWS were carried out by using two-phase anaerobic systems for they were found to be more effective in biomethanation than single-phase system [5]. However, two-phase systems are less cost-effective than single-phase system. Hence, ACR can be considered as a potential reactor for digestion of FW in batch-mode and semi-continuous mode.

The treated effluent from the reactor was not a clarified one particularly at high slurry concentrations e.g. 50%. This may pose the difficulties such as uneconomical and energy intensive transportation and squeezing of the effluent. Hence, a secondary clarifier may be provided which eventually would densify the
effluent and the reclaimed water may possibly be reused for further slurry preparation and the sludge as manure. The water may also contain the useful microorganisms which would accelerate the reaction rate, as compared to the fresh water. The biogas generation and $\text{CH}_4$ (%) content was found to be dependent on the food composition and FWS concentration.

**ACR Operation – Semi-continuous Mode**

The pH of the FWS was generally in the range of 6.5 – 7.5 and the pH of the reactor content was found to be between 7.0 and 8.0 except during same operational changes. The VFA concentration was higher at higher FWS concentration. The COD reduction and biogas generation at 3d HRT with 20% FWS concentration were found to be 93% and 0.30 m$^3$/kg COD. The ratio of total volatile acid (TVA) concentration to total alkalinity was maintained below 0.5, indicating that the reactor operation did not require additional alkalinity. Biogas generation with respect to the VSS reduction efficiency was studied and represented graphically in the Figure 1. It was observed that the biogas production was proportionate to the VSS reduction efficiency and both were constant after 120 days of operation. This has indicated that the maximum biogas production rate and VSS reduction efficiency were 0.67 m$^3$/kgVSSadded and 90% respectively.

As compared to the batch mode operation the semi-continuous operation yielded more consistent results, higher methane content and enhanced stability of operation. Hence, it may be predicted that continuous operation may lead to even better performance efficiency. However, problems related to pumping of FWS with concentration more than 10% were frequently occurring. The upflow pattern of the reactor content helped in stratification of individual type of biomass such as hydrolytic, acidogenic, and methanogenic biomass. In other words, the partial phase segregation can be possible by maintaining the upflow pattern within the column reactor. Obviously, the upflow velocity within the reactor should be maintained so that the possible phase segregation should not be disrupted. The flow pattern should preferably be maintained between laminar to turbulent flow regime. Generally, the biomethanation reactors are consisted of three phases i.e. gas phase (biogas), liquid phase (water) and solid phase (particulate matter + biomass). At high slurry concentration, the phase difference becomes conspicuous due to density difference. The density difference creates the velocity gradient between liquid phase and solid phase. The difference in velocity gradient help maintain the reactor content in suspension.

![Figure 1. Biogas production and VSS reduction](image-url)
Conclusions

The FW biomethanation was carried out in ACR without any pre-treatment reducing the cost of the bio-conversion. Semi-continuous operation was more effective than the batch mode, however, methane content in the biogas varied from 65-70% in both the modes. The efficiency of biomethanation and CH4(%) content was affected by food waste composition. The carbohydrate rich FW was the most suitable for biomethanation in view of lowest TVA production and highest biogas generation, at 3d HRT with 20% FWS concentration.

References

EFFECT OF FERROUS SULPHATE ON BIOMETHANATION AND ACCELERATION OF BIOGAS PRODUCTION FROM ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

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ABSTRACT Biomethanation is a potential method of energy recovery from OFMSW. Low methane yield due to the presence of inhibitors viz., ammonia, sulphide, etc. in the waste is a common problem of this process. Iron salt at optimum concentrations is required for methanogenic bacterial growth. The aim of the present study was to assess the effect of FeSO₄ on performance of AD. FeSO₄ concentrations from 15 to 40 mM was added to alkali hydrolysed OFMSW during methanogenesis step in a batch anaerobic digester at 30 ± 2 °C. The results of TS, VS, TOC, COD, VFA and biogas yield with or without addition of FeSO₄ were reported at 30 ± 2 °C and hydraulic retention time of 20 days. A 0.65 m³ biogas kg⁻¹ VS has been produced in presence of FeSO₄ and alkali solubilised waste without any FeSO₄ showed 0.45 m³ biogas kg⁻¹ VS under the same experimental conditions.

Keywords: Anaerobic digestion, OFMSW, FeSO₄, Biogas

Introduction

In India municipal solid waste (MSW) is mostly dumped in open sites and used for land filling. MSW of India differs greatly on composition with the MSW of western countries. On an average it consists of 50-60 % biodegradable material and C/N ratio ranges between 20 and 30. The relative percentage of organic waste in MSW is generally increasing with the decreasing socio economic status; so rural households generate more organic waste than urban households (Sharholy et al., 2008). Anaerobic digestion (AD) or biomethanation is a successful method for the treatment of organic waste (Poland and Ghosh, 1971). The overall rates of waste utilization and methane production depend on the extent to which the nutritional requirements of the methanogens and non methanogens are satisfied by constituents of the waste and by primary or secondary metabolites produced by one species and used by another (Rao and Seenayya, 1994). One of the principal issues associated with the stability of an AD process is bacterial nutritional requirements (Kayhanaian and Rich, 1995). Some additives may also affect the microbial activity of these types of microorganisms. The aim of the current work was to assess the effect of ferrous sulphate (FeSO₄) on biomethanation and acceleration of biogas production from organic fraction of municipal solid waste (OFMSW). Different concentrations of ferrous sulphate were added to well hydrolyse slurry of OFMSW and methanogenesis was conducted for each run. The results were compared with methanogenesis of slurry without addition of FeSO₄.

Materials and Methods

Feed Stock and Preparation

MSW from open dumping site of Varanasi, India was brought in small packets of 10 kg to the laboratory, opened and sorted into biodegradable fraction and non biodegradable fraction. The biodegradable fraction was mixed thoroughly using a mixer grinder in small lots and analysed for its chemical characteristics. The chemical composition is given in Table 1.

Apparatus

Round bottom flask made of glass with 2 L capacity was used. The digester had 4 opening ports which were closed with rubber stoppers. Thermometer, pH electrode and glass tube with two arms ( one arm for nitrogen purging and other arm for gas collection were inserted through 3 ports and 4th port was fitted with a dropper to adjust pH. It has an outlet valve in the right bottom for analysis of the digested material. The gas production rate was observed using a graduated 1000 ml burette filled with water by water displacement method.
Pre-treatment of Substrate

The substrate of 125 g was mixed with tap water to make slurry of 4 sets and 0.5% sodium hydroxide was added in all the sets.

Methanogenesis under Different Concentration of FeSO₄

After 6 days, cow dung slurry was added as inoculum amounting to 15 % (w/v) of total working volume of 1 L in all the 4 reactors. All bioreactors were run with same total solid (TS) concentration but different concentration of FeSO₄. One reactor was kept as control where there wasn’t any addition of FeSO₄ and it was labelled as C. All the experiments were conducted at 30-32 °C. Three different concentrations of FeSO₄ were added (15, 25 and 40 mM) on 6th day and these reactors were labelled as B1, B2, and B3. The pH of the slurry was adjusted to 7-7.2 using sodium bicarbonate (NaHCO₃) solution. The flask was closed properly so that air passage was restricted. Nitrogen gas was passed through the gas inlet port to maintain an inert atmosphere inside the bottle. The biogas produced was measured for 20 days. The effect of iron salt on the acceleration of biogas production was investigated by analysing the quantity of biogas produced along with change in parameters like volatile solids (VS), chemical oxygen demand (COD) and total organic carbon (TOC) of the substrate.

Results and Discussion

Cumulative Gas Production

Gas production analysis in the first day mainly showed carbon dioxide as the major product, because of the activity of hydrolytic bacteria. Methane production was started in all the three reactors after 3 days. The amount of biogas produced in the three reactors B1, B2 and B3 were 0.55, 0.60 and 0.50 m³/kg volatile solids, respectively and the biogas yield from reactor C was 0.40 m³/kg VS. The cumulative biogas productions with three different concentration of FeSO₄ and control reactor were shown in the Figure 1.

![Figure 1. Cumulative biogas production in all reactors](image-url)

In the reactor B3 there wasn’t any gas production after 15 days. Reactors B1, B2 and C produced biogas up to 20 days. During the last two days the biogas production was low in all the reactors.
**pH Change in the Bioreactors**

The pH was constantly checked and variation in pH was observed in all the three cases with B3 showing more pronounced effect. The pH was corrected to 7-7.2 in all the reactors by adding NaHCO₃ solution occasionally. The change in pH was shown in Figure 2.

![Figure 2. pH change with time in three reactors](image)

**Profile of VFA**

The VFA production was calculated every 4 days and it was expressed as acetic acid in mg/l. Bioreactor B1 showed VFA from 10,000-12,000 and B2 showed in the range of 8,000-10000. It was seen that amount of VFA in B3 was increased and reached a very high value of 18,200 on 15th day and after that gas production was stopped (Figure 3).

![Figure 3. Profile of VFA production](image)

High amount of FeSO₄ in the reactor must have lead to formation and accumulation of VFA in higher amount which in turn disturbed the methanogenesis process. This shows that production of VFA increased due to high iron content. Further conversion of acetic acid into methane was not taking place as expected; the reason may be due to the sulphate ion concentration exceeding the tolerable limit. It is difficult to conclude whether the competition for the substrates between sulphate reducing bacteria and methane formers or the toxicity due to sulphide is responsible for poor methanogenesis.

**Change in Chemical Composition of Waste**

The sludge left after the biogas production was analysed for TOC, COD, VS and TS. All the results are shown in Table 2. The results of study show that ferrous ions play an important role in methanogenesis. The rate of methane production was enhanced during the digestion. The enhanced methane yield during AD may be due to the presence of metal ions to activation of metalo-enzymes by the metal ions (Geetha et al., 1990). The reason for the highest amount of biogas in reactor B2 may be due to the fact that iron is present in the...
optimum amount and a higher amount of iron may lead to inhibition due to toxicity as observed in reactor B3. A total iron concentration in the medium of between 15 and 22.5 mM gave the best results for the degradation of MSW and production of methane. Due to the maintenance of strict anaerobic conditions, the hydrod氧 sulphide formed as a result of the reduction of sulphate by mixed cultures react with ferrous ions to form ferrous sulphide, which is insoluble. Sulphate addition did not inhibit methanogenesis unless greater than 100 micrograms of free sulphide per ml of water is present. Sulphate reducing organisms appear to assume the role of methanogenic bacteria in sulphate containing sediments by utilizing methanogenic precursors (Winfrey and Zeikus, 1977).

Table 2. Results of digested sludge after AD.

<table>
<thead>
<tr>
<th>Parameters↓</th>
<th>B1 Initial</th>
<th>B1 Final</th>
<th>B2 Initial</th>
<th>B2 Final</th>
<th>B3 Initial</th>
<th>B3 Final</th>
<th>C Initial</th>
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<td>22.6</td>
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Conclusions
Enhancement of biogas production from MSW is a potentially valuable route for the recovery of energy from waste. It is evident from the present study that addition of iron can increase the rate of biogas production and helps in rapid stabilization of the waste. Biomethanation of MSW in presence of iron with a view to increase biogas output is useful, provided the optimum concentration of iron is used and has adequate time for the micro organism to acclimatize to the presence of iron.

Acknowledgements
We extend our thanks to the Banaras Hindu University, India for providing us all the facilities and financial support.

References
THE INTERMEDIATE AEROBIC HYDROLYSIS: A SURVEY AND FIRST RESULTS OF THE EXPERIMENTAL PHASE

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ABSTRACT In this research project the effect of oxygen to moderately and hardly degradable components of organic waste is investigated. After a first digestion step easily degradable substances were converted into biogas whereas moderately and hardly degradable components remain. In a second step oxygen is provided to the digestate in a separated tank. Microorganisms can use oxygen to decompose high-molecular substances like cellulosates and fats. The organic fragments of this step will be recirculated into the first step. The idea was to use aerobic pathways to improve the degradation of organic material by excreted enzymes which are only produced under aerobic conditions. In a first phase a reliable fermentation system was invented which can provide the needed pre-digested material. This material was treated with different oxygen concentrations and digested afterwards. No effects could be seen up to now. If the retention time during the oxygen treatment was too low to enable the bacteria to excrete enzymes like cellulase or if the bacteria starve because of low substrate concentrations is part of recent studies.

Keywords: Biogas, Hydrolysis, Aerobic, Digestion

Introduction

Fermentation of organic material collected from municipal waste causes several problems. High yearly limit of variation and inhomogeneity due to different area structure and collecting systems can cause significant variations in biogas production during the year. Organic waste fractions content not only easy fermentable substances like proteins and starch but also cellulosates, lignocellulosates and fats. Hydraulic retention times of 10 to 15 days are necessary to convert fats [1-3]. Lignocellulosates and hemicellulosates are hardly degradable under anaerobic conditions. Lignocellulosates and hemicellulosates are inert to fermentative degradation. Using aerobic metabolic pathways the bioavailability could be increased, this is the main idea of the intermediate aerobic hydrolysis. Furthermore the separation of process steps can lead to a retention time reduced of ca.20% in the digester [4].

Installing an aerobic hydrolysis is one possibility to activate aerobic metabolic pathways. In the aerated liquid aerobic and microaerobic areas occur. Temperature of the liquid phase will arise, due to the higher metabolic activity of the microorganisms. With exoenzymes, excreted by bacteria and especially fungi, hardly degradable substrates like cellulosates and hemicellulosates can be converted into starch and other low-molecular substances. Most proteins will be cleaved into polypeptide chains and amino acids. These diffusible decomposition products are available for acidogenic and acetogenic bacteria.

First a pre-digestion step is implemented with a low hydraulic retention time to digest easy fermentable substrates as carbohydrates, proteins and fats with a low-molecular weight. To obtain a retention time below the doubling time of the methanogenic archaea retention of biomass is necessary. After the pre-digestion the effluent is aerated in a bubble column to enhance the degradation of anaerobic stabile substances as hemicellulosates and cellulosates as well as lignocellulosates by using aerobic metabolic pathways. Afterwards the aerated liquid phase is transferred into a second digester to ferment degradation products from the aerobic step. Instead of losing easy fermentable substances in a first aerobic step to heat the digester up they are saved to produce biogas. By using aerobic metabolic pathways for medium and hardly degradable components in an intermediate hydrolysis step the total biogas production should be enhanced

Materials and Methods

Continuously feed experiments were carried out in fluidized bed reactor with a volume of 10 liters to compare gas production, process stability and maximal volume load. As feeding substrate an artificial model substrate was created due to high variation of biowaste during the experimental phase. In early experiments the model substrate was tested and compared with collected biowaste. No significant difference could be proved. The first aeration experiments were carried out in a 90 l vessel. Fresh substrate
was digested for ten days and afterwards aerated for different times. The aerated digestate was mixed with fresh inoculums and digested for another 21 days.

**Results and Discussion**

*Fluidized Bed Reactor*

![Figure 6. Gas production of the fluidized bed reactor](image)

Feeding interruption on Sunday is obviously, every seventh day a great decline of gas production is measured. During the experimental phase an acceleration of gas production after feeding interruption takes place as well as a higher decrease of gas production during the feeding interruption. This is a result of the higher biomass content in the reactor. Turnover of substrates is much higher with more biomass content in the reactor, that’s why decreasing an accelerating is more marked the longer the process is carried out. Due to maintenance, pumps and heating of the reactor were shut down on day 52. After shut down the feeding rate was reduced from 4 to 1.5 g$_{\text{ODM}}$/(l fermenter *d). Rapidly rising of the feeding rate had no significant influence in the pH shown in Figure 7 as well as to VOA/TIC-ratio.

![Figure 7. Fluidized bed reactor: [A] feeding rate and pH, [B] feeding rate against gas production](image)

In contrast to the data of the fixed bed experiment, the gas production of the fluidized bed reactor is increasing with high feeding rates. As expected feeding rate and gas production are positively correlating (R$^2$=0.97), shown in Figure 7[B]. As long as no inhibition of the metabolic pathway appears gas production and feeding rate should have a constant ratio. Different reasons can change this ratio. If the hydraulic retention time is lower than time needed to convert substrates, like cellulosics, high-molecular fats, these substrates will leave the reactor before being converted into biogas. Another reason could be hydrolysis of easy digestible substrates. This would lead to an enrichment of organic acids in the liquid phase. The decreased pH-value would cause an inhibition of the methanogenic metabolic pathway with lower methane content as a result, but the gas composition was stable during experimental phase.

*Aeration Experiments*

The gas production during the pre-digestion was as high as comparative digestions in GF21 experiments. Aeration experiments of the pre-digested material with an air exchange rate of 1 m$^3$/ (m$^3$*h) were carried out.
for 8, 16, 24, 48 and 72 hours. After new inoculums were added the gas production was measured in 5 gallon flasks for 21 days, but no significant difference in the gas productions between the different aeration times could be discovered, compared to the untreated zero sample it was lower every time.

Conclusions

In case of low hydraulic retention times the fluidized bed reactor is a good choice regarding to process stability and efficiency. An up-scale is planned to provide sufficient substrate for continuous aerobic hydrolysis experiments during the next phase. Aeration experiments on the pre-digested material did not provide the expected results. If the aeration time is too short to enable bacteria to use the aerobic metabolic pathway and to produce exoenzymes will be object of further investigations, as well as experiments with special substrates, like pure celluloses, to prove the presence and activity of exoenzymes. Potentially exoenzymes are excreted form bacteria but the substrate concentration is too low for a significant gas production. Another experiment will investigate a continuously fed aerobic hydrolysis with a higher sludge age to enrich exoenzymes producing bacteria and use the effluent of this process step directly in the first digestion step.

Acknowledgements

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References

ABSTRACT  Changes of the methanogenic pathways were monitored during thermophilic anaerobic digestion of 100 mmol/L acetate at initial pH values of 5.0−6.5, using isotope signature and selective inhibition method. Lower pH extended the lag phase of methanogenesis, with 0d, 2d and 16d in the control at pH 6.5, 6.0 and 5.5, respectively. Complete inhibition of methanogenesis lasted throughout the incubation at pH 5.0. Results from two methods demonstrated, acetoclastic methanogenesis (AM) and the tandem reactions of syntrophic acetate oxidation and hydrogenotrophic methanogenesis (SAO-HM) both contribute to release of methanogenesis from acid crisis. Their relative contributions were influenced by the pH in the process. Neutral pH seemed to favor SAO-HM, with fraction of SAO-HM pathway ($f_{\text{H}_2}$) about 60% initially at pH 6.5, while only around 20−25% at pH 6.0 and 5.5. $f_{\text{H}_2}$ decreased dramatically afterwards with pH increasing to 8.0−8.5. Methanogenic conversion of acetate could initiate independently via SAO-HM when AM was inhibited.

Keywords: Methanogenesis pathway, Acid crisis, Thermophilic anaerobic digestion

Introduction

Anaerobic digestion of biomass for methane production is attracting increasing attention owing to its potential as a substitute for fossil fuels and to reduce carbon dioxide emissions. Anaerobic digestion technology is now widely applied, but in the mean time there exist various technical barriers needed to be overcome [1]. Accumulation and inhibition of volatile fatty acids (VFAs) is one of the most concerned challenges. When an anaerobic digester comes into acid crisis, it is difficult to start up or recover stable methanogenesis, since methanogens are highly sensitive to VFAs inhibitors and low pH [2]. In order to release from the acid crisis, the downstream flux for degrading the accumulated VFAs need to be strengthened.

As the most dominant intermediate for anaerobic digestion of organic matter, transformation of the accumulated acetate to methane could be conducted via two pathways, the first one is acetoclastic methanogenesis (AM), the other is the tandem reactions of syntrophic acetate oxidation (SAO) and the sequent hydrogenotrophic methanogenesis (HM), called the SAO-HM pathway [3]. It is generally assumed that 70% of the precursor for methane production is acetate and the remained 30% derives from H$_2$/CO$_2$ [4]. Nevertheless, SAO-HM pathway has been frequently observed in various methanogenic environments, especially under thermophilic or stressed conditions [5]. Our previous works revealed that a large percentage of methane was initially derived from CO$_2$ reduction, indicating the predominant contribution of the tandem pathway to acetate degradation at high concentrations [5]. However, the relative importance of these two methanogenic pathways in the release from acid crisis is still scarcely documented and quantified, especially facing to different degrees of acidification.

In the present work, to obtain insight into the mechanism for initiation of methanogenesis from acid crisis, the methanogenic pathways were monitored during thermophilic anaerobic digestion of 100 mmol/L acetate at initial pH values of 5.0−6.5. SAO-HM pathway was separated to be investigated by the application of methyl fluoride (CH$_3$F), an AM inhibitor. Stable carbon isotope compositions of CH$_4$ ($\delta^{13}$CH$_4$) and CO$_2$ ($\delta^{13}$CO$_2$) were also measured to quantify two pathway branches, combined with 16S rDNA gene cloning and sequencing to analyze the methanogenic community structure.

Materials and Methods

Source of Granules
Fresh methanogenic granular sludge cultivated in an UBF was collected as an inoculum. The UBF was stably operated at 55°C with glucose and acetate as the substrate at an organic loading rate of 2000 mg-COD/(L·day). The granules were 2–3 mm in diameter and were brownish black. Specific metabolic activity assays, including those for acetoclastic methanogenic activity, hydrogenotrophic methanogenic activity and acetate oxidizing activity, were conducted to evaluate the inoculum according to a modified version of the method described by Uemura et al [6].

**Batch Experiments**

9 sets of experiments in batch mode were initially launched. The aforementioned granular sludge was added to serum bottles at a volatile suspended solid (VSS) concentration of about 3 g/L. Sodium acetate was then added as the substrate to an initial concentration of 100 mmol/L. Phosphate buffer was used and the pH of the bulk liquid was adjusted to 5.0, 5.5, 6.0 and 6.5 with 1 mol/L HCl, respectively. The control sets with no CH₃F and AM-inhibited sets with CH₃F were conducted simultaneously. In the latter ones, CH₃F was injected into the headspace after being filled with N₂, and then mixed by manually shaking. One set without acetate addition was conducted to evaluate endogenous methane production as the blank. All reactors were incubated statically at 55°C in darkness. Liquid and gas samples were taken periodically for analysis until the added acetate was exhausted.

**Sample Analysis**

The process performance was monitored by measuring biogas production and composition, liquid pH, VFAs, total organic carbon (TOC) and total inorganic carbon (TIC) concentrations. The methanogenesis pathway was determined by measuring the stable carbon isotope signatures of CH₄ and CO₂. Detailed analysis method for these parameters referred to [5]. Archaeal clone library were generated from polymerase chain reaction (PCR)-amplified 16S rDNA the archaeal primers 1Af (5' -TCY GKT TGA TCC YGS CRG AG-3') and 1100Ar (5' -TGG GTC TCG CTC GTT G-3'). The detailed procedure was described in reference [7].

**Thermodynamics Calculation**

Gibbs free energy values (ΔG) for acetate oxidation and CH₄ production from acetate and H₂/CO₂ were calculated from the actual concentrations of the reactants and products using Nernst’s equation as follows:

\[
\Delta G_{AO}^\prime = \Delta G_{AO}^\theta + RT \frac{[HCO_3^-][pH_2]^4}{[CH_3COO^-]} 
\]

\[
\Delta G_{AM}^\prime = \Delta G_{AM}^\theta + RT \frac{[pCH_4][HCO_3^-]}{[CH_3COO^-]} 
\]

\[
\Delta G_{IM}^\prime = \Delta G_{IM}^\theta + RT \frac{[pCH_4]}{[pH_2]^4[HCO_3^-]} 
\]

Values of the standard Gibbs free energy (ΔG⁰) were corrected for 55°C according to Lee and Zinder [8]. The detailed assessment of stable carbon isotope fractionation refered to [5].

**Results and Discussion**

Specific activity assays showed that acetoclastic and hydrogenotrophic methanogenic activities of the inoculum were 272 and 104 μmol-CH₄/(h·g-VSS), respectively. These results indicated that acetate-cleaving and H₂-utilizing methanogens were both enriched in the studied sample granules, which was further confirmed by the archaeal 16S rDNA clone library analysis. In the acetate oxidizing activity test, the hydrogen partial pressure (pH₂) in the test vial with methanogenesis blocked by 2-bromoethanesulfonate increased to around 40 pa dramatically in the first 8 d, while that in the blank rose slowly and remained much lower in the initial period (Figure 1a). Accumulation of H₂ in the headspace
validated the existence of the syntrophic acetate-oxidizing bacteria and the reaction could even occur without the participation of H$_2$-consuming methanogenesis.

Figure 1. (a) Hydrogen partial pressure (pH$_2$) in the specific activity assays (b) Acetate conversion rate ($r_a$) under different initial pH and CH$_3$F additions

With monitoring the stable carbon isotope compositions of the biogas, the effective separation of SAO-HM by CH$_3$F addition was verified since the $\delta^{13}$CH$_4$ in the AM-inhibited sets was much more negative (around $-60\%$ to $-80\%$) than that in the control sets (around $-30\%$ to $-60\%$). The evolution of acetate conversion rate ($r_a$) showed that lower pH extended the lag phase of methanogenesis, with 0d, 2d and 16d in the control at pH 6.5, 6.0 and 5.5, respectively (Figure 1b). While, methanogenic conversion of acetate could initiate independently via SAO-HM, albeit later and more slowly. Complete inhibition of methanogenesis lasted throughout the incubation at pH 5.0, with methane not detected and only traces acetate consumed.

Isotope analysis in the control demonstrated that the fraction of SAO-HM pathway ($f_{112}$) was about 60% initially at pH 6.5, while only around 20–25% at pH 6.0 and 5.5. $f_{112}$ decreased dramatically afterwards along with pH increasing to 8.0–8.5. Neutral pH seemed to favor SAO-HM. pH$_2$ increased vigorously accompanied by the start-up of methanogenesis and was much higher in the AM-inhibited sets, implying more active SAO reaction than in the control. While, increasing pH$_2$ rendered HM more feasible, but made SAO thermodynamically difficult to proceed (Figure 2).

Figure 2. Gibbs free energy ($\Delta G$) for acetate oxidation (●, ○), hydrogenotrophic methanogenesis ( ▼, △) and aceticlastic methanogenesis (■, □) at (a) pH 6.5, (b) pH 6.0 and (c) pH 5.5 sets with closed symbols for control sets and open symbols for CH$_3$F treated sets.
Conclusions
Results from selective inhibition and isotopic signature demonstrated that, AM and SAO-HM both contribute to release of methanogenesis from acid crisis, and their relative contributions be influenced by the pH in the process. Neutral pH seemed to favor SAO-HM. Methanogenic conversion of acetate could initiate independently via SAO-HM when AM was inhibited. Our study further confirmed the importance of SAO-HM pathway and suggested that acid crisis under thermophilic anaerobic digestion could be alleviated through intensifying the SAO-HM pathway, especially when AM be supressed.

Acknowledgements
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References
ABSTRACT AWN Umwelt GmbH is currently establishing a mechanical biological treatment plant for municipal solid waste in Gaobeidian (PR China). The plant has a capacity of 40,000 Mg/year. The major objective was the segregation of recyclables, the production of stabilized biomass and the avoidance of methane gas from the landfill. The reduction of the greenhouse gas methane amounts to more than 35,000 Mg CO₂eq per year. The facility will start operation in summer 2011.

Keywords: Waste treatment, CDM, Methane Oxidation, GHG, Landfill

Introduction

Experts estimate that 8 to 12 % of greenhouse gas (GHG) emissions in developing countries are due to waste management activities [1]. The major sources are methane emissions from disposal of untreated municipal solid waste. Biological waste treatment is an effective technology to stabilize organics and to minimize decay processes in landfills. The MBT plant in Gaobeidian is a pilot waste management project to demonstrate this technology in China and is co-financed by the International Climate Initiative (IKI) of the German Ministry of Environment, Nature Conservation and Nuclear Safety. The project is administered by AWN Umwelt GmbH, a German waste management company partly public owned by Abfallwirtschaftsgesellschaft Neckar-Odenwald-Kreis based in Buchen.

Method

Between 2006 and 2008 a feasibility study was carried out, which was funded by the PPP facility of the KFW development bank, an endowment fund for the support of public private partnership projects financed by the German Ministry of Economic Cooperation and Development (BMZ). Various technical investigations were conducted by experts from Technical University Braunschweig, AWN Umwelt and Pöyry Environment Witzenhausen. Data on waste generation and waste composition were examined. The composition of the waste was determined by hand assorting. The samples were screened by 40 mm and 10 mm sieves. The sieve overflows were sorted into groups of materials. Table 1 shows the waste composition distinguished by materials.

The suitability of the potential biological treatment procedures under the given boundary conditions (local situation, climate, waste composition) was examined in three different pilot plants: The results confirmed that the biological treatment was suitable. The output material meets the German standards for waste disposal. The respiration activity measured as AT₄ (respiration during 4 days) dropped significantly down from 25 to 1,9 mg O₂/kg after two weeks of treatment reflecting the comprehensive stabilization of the organics. Though the quality of output material was welcomed, the total mass of converted organics was small due to low input concentration. For the large scale application it was anticipated to increase the portion of organic in the input.
material by either segregating non-organic waste or by separation of organic waste before treatment. Since a separate source collection is not feasible in Gaobeidian a test was carried out for hand assorting of organic materials. A biowaste acquisition campaign was launched at the dumpsite. During a period of 5 weeks biowaste was accepted against payment and has been placed immediately on the composting heap. Larger quantities of biowaste were delivered by both waste pickers and residents at a rate of 6 €/t.

Based on the technical investigations a predesign was prepared for a mechanical-biological treatment plant (MBT) by Pöyry Environment Witzenhausen. The MBT plant consists of a mechanical and a biological treatment step. The mechanical treatment aims on segregating of valuable goods (paper, synthetics) and on enrichment of the organic fraction.

![Figure 2. Lay out of the MBT Gaobeidian](image)

After the mechanical treatment the waste is directed to a biological treatment. The output (stabilized biomass) may be used as compost, for landfill cover or soil amendment. Excess material will be disposed to the landfill. The biological treatment will be carried out as an aerobic, actively ventilated stabilization. The process will be carried out partly under roof and partly in open air areas. The triangular windrow heaps will be frequently turned by means of mobile equipment. The annual treatment capacity amounts to 40,000 t. The capacity can be significantly increased by introducing two working shifts. The location still provides contingency area for an expansion of the biological treatment. Figure 2 illustrates the lay out of the facility.

### Results

The generation of methane in the landfill will be dramatically reduced by disposing stabilized biomass instead of untreated waste. The emission reductions were calculated using the methodologies of UNFCCC, which are relevant for CDM projects. Since the facility has been financed by national revenues from carbon trade a registration as CDM project is not permitted. The methodology AMS III.F (Avoidance of methane production from decay of biomass through composting) serves as the base of the baseline study and the monitoring concept. For the calculation of the methane emissions by the disposed waste, a biological decay of the deposited waste is modelled.

Table 2 shows the provisional calculated emission reductions of 83,812 t CO₂eq for the project period of 2012-2021. In case that the planned measures to increase the organic fraction and the utilization of MBT output for methane oxidation layer (MOL) are implemented, the total emission reduction may increase to more than 350,000 t CO₂-equivalents. The calculation considers covering of 2 ha landfill surface per year with a methane oxidation layer utilizing 20,000 t stabilized biomass from the MBT.

### Conclusion

On 3rd of July 2009 the construction of the MBT was officially launched in a ceremony by laying the first stone. The execution of the project proceeds quickly. In accordance with the Chinese regulations a feasibility study and an environmental impact assessment was carried out. The official approval was
granted by November 2009. Site clearance and construction of access and supply infrastructure was launched immediately but suffered from harsh weather conditions in winter 2010. The main construction works of the facilities started in April 2010 and is close to completion (Figures 3 and 4). The construction works are expected to be finalized by summer 2011.

Table 2. Emission calculations, emission reductions (ER) in Mg CO₂eq

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Acknowledgements

The project developers appreciate the funding from the International Climate Initiative (IKI) by German Federal Ministry of Environment, Nature Conservation and Nuclear Safety. The International Climate Initiative is financing climate protection projects in developing and newly industrialising countries since 2008. Through this, the Federal Environment Ministry is making an effective contribution to emission reductions and adaptation to climate change. Funding of 120 million euro per year is available for the International Climate Initiative from the revenues of the sale of emission allowances. When selecting projects, great importance is attached to the development of innovative and multipliable approaches that impact beyond the individual project itself and are transferable.

References

FOOD WASTE HYDROLYSIS IN SLS-CSTR UNDER LOW ORGANIC LOADING RATE: EFFECT OF pH UPON METABOLITE DISTRIBUTION

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ABSTRACT The present research was intended to develop a new solid liquid separating CSTR (SLS-CSTR) with the main aim of retaining active biomass for effective hydrolysis/acidogenesis of food waste and also to provide the higher solid with lesser hydraulic retention time (SRT and HRT). Two SLS-CSTRs were designed for the purpose with the working volume of 3.7 L and very low organic loading rate (OLR) of 2 gVS/L/day was employed. One reactor was maintained under acidic (pH=6) and another one under alkaline (pH=9) conditions using sodium hydroxide (NaOH) for the optimization purpose. The enzyme amylase, protease and β-galactosidase activities were measured during this period and were comparable with the organic leaching and acidification rate. The study results proved that the design was appropriate and can achieve better hydrolysis rate (2.1 gVFA/L) under alkaline pH, which can be easily further biomethanized in second stage UASB reactor.

Keywords: Food Waste, Hydrolysis/acidogenesis, CSTR, Organic loading rate, pH and enzymes

Introduction

A two-phase anaerobic digestion (AD) system, which separates hydrolysis/acidogenesis (Hy/Ac) from methanogenesis processes, is a more attractive and highly competent technology for treating food waste than single stage AD system [1]. Most commonly, CSTRs were employed for Hy/Ac for various biodegradable components like, food waste, fruite and vegetable waste, organic fraction of municipal solid waste, under various organic loading rates (OLR) ranged between (0.1-7.0 gVS/L/day). According to EPD [2], food waste constitute about 35% (i.e., around 2,200 tones per day) of the municipal solid waste in Hong Kong and which pose high methane emission potentials of 200 to 500 L-CH4/kg VS [3 & 4]. But, a very low pH and high concentration of volatile fatty acids (VFAs) production during Hy/Ac offer unique challenges in methane production stage and therefore it is essential to maintain high ratio of active biomass for preventing irreversible acidification within the first stage Hy/Ac reactor. Further, Hy/Ac of food waste required longer SRT and lesser HRT. Therefore, optimization of Hy/Ac process for stable VFA production is essential for the maintenance of efficient production of methane during methanogenesis stage of AD. Considering these predicament, bench scale CSTR reactors were designed for Hy/Ac of food waste to meet the objective of decoupling SRT and HRT in same reactor for effective VFA production. The operational variables such as pH changes and agitation/mixing rates were set during the reactor optimization study and results are discussed.

Materials and Methods

Simulated food waste with the TS content of 39.5 % with volatile solid (VS) content of 97.1 % was used in the present study. Two CSTR was designed with the total and working volume of 6 and 3.7 L, respectively (Figure 1a). To provide liquid solid separation in CSTR, 3 mm mesh screen was designed cylindrically with the height of 28cm and dia 6.5cm and placed inside the reactor for decoupling SRT and HRT (Figure 1b). The reactors were initially loaded with 1 kg of simulated food waste mixed with anaerobic UASB sludge (500 mL) and 1 L water. The contents were continuously mixed with the help of stirrer (600 rpm) and daily pH variations were monitored. Leachate samples (50 mL) were collected once in four days for characterization and calculating acidification rate without feeding. After 10 days, semi-continuous feeding was initiated with the content pH adjustment to acidic (pH=6) and alkaline (pH=9) range in SLS-CSTR 1 and 2, respectively. The organic loading rate of 2 gVS/L/day was studied in both the reactors and NaOH was used for continuous pH adjustment. Later on, the agitation speed was set to 300 rpm in SLS-CSTR 1 and 2 and monitored for acidification rate. Daily 100 mL of the leachate was collected for methanogenesis and replaced with 100 mL of distilled water. The samples were grabbed for physic-chemico-biological analysis. Experiments were run for totally 90 days under controlled room temperature (35°C).
Results and Discussion

The acidification rate and organic leaching properties were similar for the first 10 days period, indicated the substrate homogeneity and comparable reactor functioning. The pH was in the range of 3.5-4.2 and conductivity values varied between 2.35 and 5.36 mS/cm during this period. Aforementioned, the reactors were shifted to semi-continuous mode of operations under regulated pH conditions of 6 and 9 using alkali addition every day after initial start-up. Maximum of 3.5 and 8 g of NaOH were consumed respectively for SLS-CSTR 1 and 2, during initial tuning period with 600 rpm agitation. Later, while 300 rpm agitation employed, the consumption was comparatively less i.e., 1.8 and 3g in SLS-CSTR 1 and 2, respectively, due to reactor stability from long run. Whereas, NaOH additions were influenced the reactor alkalinity and produced leachate with high EC values in both the reactors. But on the other hand continuous decoupling of HRT (= 1 day) from SRT (> 1 day) with daily water replacement provided washout effect, therefore not more than 18 and 27 mS/cm of EC values were recorded in SLS-CSTR 1 and 2, respectively.

Organic leaching and acidification rate

Leaching behavior of total organic carbon (TOC) and acidification rate in terms of total volatile acid production (tVFA) were depicted in Figure 2a and b, respectively. The results showed that the alkaline pH condition from SLS-CSTR 2 was leaching out more TOC and VFA than the acidic pH condition employed in SLS-CSTR 1. During initial start-up period, maximum of 27-28 g/L of TOC were leached with the tVFA accumulation of 4.5g/L in SLS-CSTRs. With the higher agitation rate with semi-continuous operation and leachate replacement led to more wash out of organic particulates in both the reactors. Even though, the tVFA production were increased gradually with the active biomass retaining capacities of the reactor under 600 rpm, which served the purpose design, it would be better to reduce the agitation rate for energy saving purpose.

Under 300 rpm, the TOC leaching was around 14.5 and 16.5 g/L in SLS-CSTR 1 and 2, respectively. The tVFA productions were ranged between 1.35 and 19.8 for SLS-CSTR 1, whereas bit higher in range between 16.8 and 25.1 for SLS-CSTR 2 were recorded. As overall, the SLS-CSTR2 produced more acidified leachate with acetic and butyric acids as the major species in tVFA, which is complimentary for methanogens in later stage. Whereas, the SLS-CSTR 1 produced more of acetic acid along with valeric and caproic acids as the major tVFA species.

Enzyme activity measurement

Enzyme amylase showed maximum units/mL of leachate than the β-galactosidase and protease in the present study. During initial start-up periods, the amylase activity measured between 3 and 4 U/mL in both the reactors and later it reduced to 1.5 U/mL with irrespective of pH and agitation conditions. Whereas, β-galactosidase activity was measured as 1.3-1.5 U/mL initially in both the reactor and later it showed better activity i.e., 3.5 U/mL with SLS-CSTR 2. Agitation speed adversely affecting the β-galactosidase
activity in both the pH condition was clearly evident from the study results. Similarly, enzyme protease activity was much better in SLS-CSTR under 300 rpm.

Figure 2. Leaching behavior of TOC and tVFA from SLS-CSTRs

*Microbial quantification using RT-PCR*

Total bacterial count, lactobacilli and methanogen populations were monitored using RT-PCR studies in SLS-CSTRs. The reactors were initially seeded with methanogenic sludge from UASB reactor as inoculum for initial startup. Therefore, the first day samples showed methanogen counts (5.6*10^2) in SLS-CSTRs and completely nil results after that. Similarly, lactobacilli were dominated during initial start-up period and later on showed less counts in SLS-CSTR2. Total bacterial activity was maximum (8.9 – 9.6*10^3) during low agitation of 300 rpm in SLS-CSTR corresponded with TOC and VFA leaching pattern.

**Conclusions**

From the study results, a newly designed SLS-CSTR successfully served the purpose of SRT and HRT separation with maximum tVFA production from food waste. Alkaline pH condition (SLS-CSTR 2) with lower agitation speed (300 rpm) provided consistently high tVFA with acetic and butyric acid as the major species. The active biomass retained with in the SLS-CSTR was comparatively higher than the normal CSTR reactors.

**References**

EFFECT OF INOCULUM TO SUBSTRATE RATIO ON THE HYDROLYSIS AND ACIDIFICATION OF FOOD WASTE IN LEACHBED REACTOR

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Abstract: Appropriate inoculum to substrate (I/S) ratio can enhance the hydrolysis of particular organic matter and reduce the solid retention time. Due to the faster growth rate of acidogens than methanogens, it is reasonable to expect a lower demand of I/S ratio in the acidogenic reactor. Three I/S ratios were evaluated in the laboratory scale acidogenic leach bed reactors (LBR), i.e. 20, 40 and 80% (w/w basis), respectively. Results indicate that the higher ratio of I/S lead to higher hydrolysis rate of protein, whereas a similar decomposition rate of carbohydrate in all LBRs. After 17 days of digestion, COD (chemical oxygen demand) leaching rates were quite similar, ranging 33.8 - 38.8 g/kg VSadded/d. As a result, differences among three I/S ratios in volatile solids (VS) removal efficiencies were marginal, i.e. 65.2, 68.2 and 71.7% for LBR_20, LBR_40 and LBR_80, respectively. Results indicated that the effect of higher ratio of I/S was insignificant in enhancing the overall hydrolysis rate of food waste in LBR and therefore, a lower I/S ratio of 20% was recommended to be used in the hydrolytic-acidogenic process of food waste from the financial perspective.

Keywords: Food waste, Hydrolysis, acidogenesis, Inoculum to substrate ratio, Leachbed reactor

Introduction

The demands for reduction and effective utilization of municipal solid waste (MSW) have increased immensely for Hong Kong SAR in recent years due to the limited landfill resources. Anaerobic digestion of sorted organic fraction of MSW, especially food wastes, is the utmost attractive alternative and the most cost-effective technology. Anaerobic digestion of organic matter is generally considered to be a two-stage process in which the acidogenesis and methanogenesis are in dynamic equilibrium [1]. Therefore, a two-stage anaerobic digestion system, constituting leach bed reactor (LBR) and upflow anaerobic sludge blanket (UASB) that can separate acidogens and methanogens spatially to regulate the imbalance between two groups of microbial communities seems an attractive design. In the start-up of LBR, an appropriate ratio of inoculum to substrate (I/S) can not only enhance the hydrolysis of particulate organic matter, but also significantly reduce the operation time, and consequently reduce the volume of digester [2]. However, previous studies on I/S are mostly carried in the single-stage methanogenic reactor [3, 4]. Due to the higher growth rate of acidogens than methanogens [5], it is reasonable to consider that the requirement of inoculums amount in the separated acidogenic reactor should be lower than methanogenic reactor. Therefore, the aim of the present study was to investigate the effects of initial I/S ratio on the decomposition rate of food waste in hydrolytic-acidogenic LBR.

Experimental set-up and Analyses

The composition of food waste, source of inoculum and the reactor design were described previously [6]. Briefly, synthetic food waste with a total solid (TS) content of 38.5% with volatile solid (VS) content of 97.1% was used as the substrate; while sludge having 3.8% of TS and 85.2% of VS/TS was used as inoculum. Concerning the reactor, each system consisted of an acidogenic LBR with a working volume of 4.6 L and a methanogenic UASB reactor with a working volume of 10.0 L. Three volumes of inoculum, i.e. 200, 400 and 800 ml, and 75 g wood chips (bulking agent) were mixed with 1.0 kg food waste and loaded into each LBR. Then 1.0 L of tap water was added into LBR on day 0. Leaching occurred naturally and the leachate was collected at the bottom chamber of the LBR daily. Exactly 50% of the collected leachate was adjusted to pH 6.0 and recycled into LBR as the pH adjustment enhanced the chemical oxygen demand (COD) yield in our previous study [6]. The samples collected were analyzed for pH, COD, volatile fatty acids (VFA), ammoniacal nitrogen (NH₄⁺-N) and total Kjeldahl nitrogen (TKN) as described in a previous study [6]. Experiments were run for 17 days under controlled room temperature (35°C) with two replicates for each experimental condition. Therefore the reported results are mean ± standard deviation of two independent analyses.
**Results and discussions**

pH is an important parameter that could affect the bacterial activity and metabolite pathways. In this experiment, daily pH adjustment of the recycling leachates with sodium carbonate increased the pH values of LBRs gradually from initial values of < 4.5 to > 5.5 after 8 days as observed in previous reports [6] (Fig. 1). Further, a pH of ~5.5 was more favorable for the hydrolysis and acidogenesis [7]. The pH variations of three LBRs were quite similar, but lower values were observed in LBR_80, might due to the higher production of VFA in LBR_80. As shown in Fig. 2, the maximum VFA concentration in LBR_80 was 11.7 g COD/L, while they were only 8.9 and 7.6 g COD/L for LBR_40 and LBR_20, respectively.

![Figure 1. (a) pH, (b) COD and VFA, (c) NH4+-N and (d) TKN of leachates from LBRs with different I/S ratios](image)

Differences among three I/S ratios in COD production were marginal as seen from the cumulative COD (Fig. 1b) and COD leaching rate (Table 1). The increase in VS removal efficiencies with increasing I/S ratio were also insignificant, i.e. 65.2, 68.2 and 71.7%. However, higher concentrations of NH4+-N and TKN were observed in the LBR_80 and LBR_40 than LBR_20 (Fig. 1c-d). These results indicate that the higher ratio of I/S lead to the higher hydrolysis rate of protein, whereas a similar decomposition rate of carbohydrate in all LBRs. A high population of proteolytic bacteria was observed in the anaerobic digested sludge [8]. However, the proteolytic organisms were apparently washed out of continuous culture at pH below 6 [9], which lead to the decrease of NH4+-N and TKN concentrations in leachate during digestion process. Nevertheless, a group of fast growing acidogenic bacteria were selectively survived and predominant in the acidogenic reactors, which are capable of degrading carbohydrates to give hydrogen with mainly acetate as soluble product [10]. As a result, quite similar COD leaching rates were obtained in present study, i.e. 33.8, 35.3, 38.3 g/kg VS<sub>added</sub>/d.

![Table 1. Decomposition kinetics of food waste in LBR with different initial I/S ratios](table)

As presented in Table 1, specific VFA yield from LBR_80 was 73% higher than LBR_20. Hydrolysis rather than acidogenesis was found to be the rate-limiting step in anaerobic digestion [1]. However, in the present study, higher acidogenesis rates were observed in LBRs with higher I/S ratio, which might be related to the peptide degradation and the activities of acidogens. Fig. 2 shows the VFA concentration and the dynamics of VFA speciation in LBRs during digestion. Acetate and butyrate were the dominant species of VFA in LBR_20, while acetate, propionate and butyrate dominated in LBR_40 and LBR_80. A switch from...
butyrate to propionate production as the pH increased was attributed to a change in the dominant microbial population, or the metabolic pathway change within the same bacterial population [11].

To our knowledge, the effect of I/S ratio in the acidogenic reactor was rarely studied. Furthermore, the values of I/S ratio used in existing studies were widely dispersed. I/S ratio of 30% weight/weight (w/w) for the acidogenic fermentation of organic urban wastes was suggested [12], whereas 0.02 (vs/vs) for manure [13], 1.0 (vs/vs) for grass [14] and 0.13 (vs/vs) [15] for food waste were also reported. In this study, I/S ratio applied in LBRs were equal to 0.03, 0.06 and 0.11 (vs/vs), respectively, which are comparable to the reported values [13, 15]. However, present results showed that the increase of initial inoculum amount did not make significant contribution to the liquefaction rate of food waste in LBR. Furthermore, if the I/S ratio was increased to 1.0 (vs/vs), a large quantity of inoculum should be added due to the high VS content of food waste, which will reduce the efficient space for waste. Therefore, relatively low quantity of inoculums would be recommended.

Conclusions

Present study found that higher inoculum addition enhanced VFA production but not the liquefaction rate and COD leaching from food waste decomposition. Thus, from a financial perspective, the lower I/S ratio of 20% (w/w) during hydrolytic-acidogenic process is recommended.

References


ANAEROBIC DIGESTION OF ORGANIC WASTE – EXPERIENCE WITH DIFFERENT SYSTEMS

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ABSTRACT Over the last 25 years, REMONDIS has invested more than 20 billion Euros in water supply and waste management facilities, a significant part of it in the field of organic waste treatment. Today, REMONDIS collects and processes yearly more than 2 millions tons of organic wastes which are mainly used for the production of fertilizers or for the transformation into energy, the latter both through aerobic and anaerobic digestion plants. Currently, REMONDIS operates nearly 60 composting plants and over 20 biogas plants worldwide; many more are under construction or in project phase respectively. The applied technologies are diverse depending on local conditions and waste streams, so that REMONDIS has a long time experience with different technical systems and processes. Based on this experience, expertise regarding the designing, building and operating of this kind of facilities enables REMONDIS to choose and install the most appropriate treatment technology at any location worldwide.

Keywords: Biogas, Biomass, Digestion, Recycling, Organic waste

Introduction

REMONDIS AG & Co. KG is a leading international water and environmental service company with over 500 branches and associated companies in 28 countries in Europe, Asia and Australia. Across the world, REMONDIS provides professional services to more than 20 million individuals and thousands of companies.

Being a part of the RETHMANN Group, REMONDIS with an annual turnover of 5.6 billion Euros and around 20.000 employees worldwide, is one of the world's largest water and environmental service companies. It has over 500 locations in 28 countries on three continents. Our primary goal is to provide professional services leading to the economical and efficient use of natural resources. With this target in mind, we are active within the area of water supply and sewage treatment, we recover raw materials from waste, we develop innovative recycling products and we supply alternative forms of energy. And through this same commitment, we use eco-friendly methods to dispose of residual waste and hazardous materials which cannot be recycled either for ecological or economical reasons. Using the many years of experience of our traditional, family-run company, we are constantly working towards improving our services, implementing innovative recycling processes and perfecting material flow management. Large knowledge, integral solutions and forward-thinking ideas are the basis of our successful business.

Organic waste treatment

In the last 25 years, interest in the recycling of organic waste has grown significantly in Europe. Scientific analysis show the lack of organics in a great part of agricultural soils in most European countries. Therefore, environmental authorities and institutions within the European Union intensively discuss and encourage their member states to improve soil conditions. In different nations such as the Netherlands, Austria, Denmark and Germany, a separate collection systems of bio-waste has been implemented over the last couple of years. Composting and using organic material for generating green energy obviously becomes more and more interesting in this business sector.

The development of different technologies is related to market expectations, expertise and research funds and economical justification. Based on these requirements, different organic waste treatment technologies have been developed. Today, more than 10 different composting systems in nearly 60 plants are used within the REMONDIS Group. Due to its market position, REMONDIS has access to different systems and technologies. This enables us to compare the efficiency of different technologies, to detect possible imperfections and to improve each system to the local requirements. A team of experienced engineers continuously improves and advances existing technologies or creates new treatment systems in order to
meet the requirements of an emerging market. Doing so, REMONDIS closely cooperates with local specialists who contribute their knowledge of processes and various system applications.

The growth of the organic waste treatment market obviously has to be supported by legislative changes in order to promote the best available technologies (BAT) and encourage research and development. A close cooperation with public authorities leads to the legal and economical support and promotes a development of not only simple but also more sophisticated technologies. Economical encouragement established in Germany in the last two decades paved the way for the creation of state-of-the-art technologies and solutions such as anaerobic treatment of organic wastes. In this context, the ecological effects of organic waste treatment are even more important as they are also a contribution to the reduction of CO₂ emissions by producing green energy – biogas.

Here are the main reasons which encourage us to invest millions of Euros in new technologies and treatment facilities.

**Anaerobic digestion**

The development of anaerobic digestion facilities started much later than those for the process of composting. Nevertheless, the effects, mostly ecological, are much more important. During the digestion process, biogas is produced and this gas can be widely used; it replaces:

- petrol for refueling cars and buses,
- coal for heat and energy production,
- natural gas for municipal gas supply.

As the biogas is generated from waste, it is considered as green energy and its use contributes to the reduction of the greenhouse effect.

The choice of organic wastes treatment technology depends on the waste stream. The input quality – municipal solid waste (MSW), separately collected bio-waste, catering and kitchen waste or the waste water (from communal or food production industry dewatering systems) – makes the most crucial difference for the choice of technology and the further use of product generated out of this kind of waste. Wet digestion is commonly used for water sludge and industrial waste treatment whereas for municipal organic waste, a dry treatment system is considered to be more appropriate (Table 1).

A product in an anaerobic treatment plant is first of all a biogas. Its quality depends on the input that table 2 presents. The crucial parameter is methane content. Starting from the material parameters and being aware of the limitation of different treatment systems, REMONDIS creates solutions with the best possible ecological effects and most economical figures at the same time. Within our organization, many specialists for design, calculation, project and construction work closely together and can draw upon many years of experience. As a result, we now have not only a wide experience of external technologies, but are able to prepare and operate our own concepts and plants.

The aim of REMONDIS is not only to spread its know-how in project, planning, construction and operation of organic waste treatment plants but also to support our international partners in this particular field of waste management. The use of biogas is an extraordinary challenge. The feed-in of biogas into municipal gas networks after separation of CO₂ with biogas processing steps is the most energy efficient pathway of use. There are examples to use biogas in CHP units on-site but also to transport the processed gas to external CHPs or customers respectively. In most of the cases, as the plant works with waste and their quality might differ over the year, the gas needs to be cleaned and conditioned in order to fulfill any kind of environmental restrictions. The most common way today is the utilization in CHP plants to produce electric power and heat for external consumers. Depending on the localization of the plant, the extend of heat utilization might be limited.

Biogas and heat use are the most important issues when it comes to the economical effect of a plant. However, the promotion of organic fertilizers and the entire sale service must not be neglected. REMONDIS understands that sale service should – among others – allow farmers and gardeners to find out the most appropriate way to use organic fertilizers and improve the soil quality. Certified products sold under the REMONDIS brand mark RETERRA assure high quality standards. Close cooperation between
compost producers and local authorities are crucial for the establishment and implementation of clear rules and transparent laws.

Table 1. Overview of RETHMANN Group (REMONDIS and SARIA) digestion plants

<table>
<thead>
<tr>
<th>Location</th>
<th>Input</th>
<th>Digester type / system</th>
<th>Capacity Mg/a</th>
<th>CHP Electric Power</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peine</td>
<td>separate collected biowaste</td>
<td>dry process digester</td>
<td>10.000</td>
<td>0.38 MW</td>
<td>1997</td>
</tr>
<tr>
<td>Wüscheim</td>
<td>separate collected biowaste</td>
<td>dry process digester; horizontal reactor</td>
<td>10.000</td>
<td>0.46 MW</td>
<td>1997</td>
</tr>
<tr>
<td>Frankfurt /M</td>
<td>separate collected biowaste</td>
<td>dry process digester; horizontal reactor</td>
<td>34.000</td>
<td>0.5 MW</td>
<td>1999</td>
</tr>
<tr>
<td>Freiburg</td>
<td>separate collected biowaste</td>
<td>dry process digester; vertical reactor</td>
<td>30.000</td>
<td>1.7 MW</td>
<td>1999</td>
</tr>
<tr>
<td>Genthin</td>
<td>Food waste</td>
<td>2 stage wet digestion fermenter 2x3000m³</td>
<td>73.000</td>
<td>1.9 MW</td>
<td>1999/2006</td>
</tr>
<tr>
<td>Deisslingen</td>
<td>separate collected biowaste</td>
<td>single stage wet process</td>
<td>22.000</td>
<td>0.84 MW</td>
<td>2003/2005</td>
</tr>
<tr>
<td>Münster</td>
<td>MSW</td>
<td>dry process digester; vertical reactor</td>
<td>24.000</td>
<td>0.47 MW</td>
<td>2003</td>
</tr>
<tr>
<td>Kogel</td>
<td>Food waste</td>
<td>2 stage wet digestion fermenter 2x2600m³</td>
<td>45.000</td>
<td>1.9 MW</td>
<td>2004</td>
</tr>
<tr>
<td>Mülheim</td>
<td>separate collected biowaste</td>
<td>wet process digester</td>
<td>24.000</td>
<td>0.65 MW</td>
<td>2005</td>
</tr>
<tr>
<td>Schwallungen</td>
<td>Food waste</td>
<td>2 stage wet digestion fermenter 2x3500m³</td>
<td>65.000</td>
<td>1.9 MW</td>
<td>2006</td>
</tr>
<tr>
<td>Neunburg</td>
<td>Industrial wastewater and organic residue</td>
<td>wet process</td>
<td>290.000</td>
<td>0.35 MW</td>
<td>2006</td>
</tr>
<tr>
<td>13.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Altentreptow</td>
<td>wastewater</td>
<td>wet process</td>
<td>970.000</td>
<td>0.71 MW</td>
<td>2006</td>
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<tr>
<td>16.500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Machin</td>
<td>Food waste</td>
<td>2 stage wet digestion fermenter 2x3500m³</td>
<td>55.000</td>
<td>2.0 MW</td>
<td>2007</td>
</tr>
<tr>
<td>Valencia</td>
<td>wastewater</td>
<td>wet process</td>
<td>180.000</td>
<td>Gas into stream vessel</td>
<td>2007</td>
</tr>
<tr>
<td>7.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Senftenberg</td>
<td>wastewater</td>
<td>wet process</td>
<td>6.800</td>
<td>0.57 MW</td>
<td>2009</td>
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<td>Ennigerloh</td>
<td>separate collected biowaste</td>
<td>dry process digester</td>
<td>10.000</td>
<td>0.68 MW</td>
<td>2010</td>
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<tr>
<td>Mönchengladbach</td>
<td>wastewater</td>
<td>wet process</td>
<td>150.000</td>
<td>Gas into stream vessel</td>
<td>2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca. 7.000</td>
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</tr>
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</table>
Table 2. Exemplary substrates and their biogas generation potential [1]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dry Solids</th>
<th>organic Dry Solids</th>
<th>Biogas Field</th>
<th>Methane kontent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DS [%]</td>
<td>oDS [%]</td>
<td>[m³/Mg oDS]</td>
<td>[%]</td>
</tr>
<tr>
<td>Bio-Waste (garden/green waste + kitchen Waste)</td>
<td>35-40</td>
<td>65-70</td>
<td>400-450</td>
<td>100-120</td>
</tr>
<tr>
<td>Organic fine fraction MSW (&lt; 50 mm)</td>
<td>55-60</td>
<td>50-55</td>
<td>350-400</td>
<td>96-121</td>
</tr>
<tr>
<td>food waste wet</td>
<td>14,4</td>
<td>81,5</td>
<td>642,6</td>
<td>75</td>
</tr>
<tr>
<td>food waste fat rich</td>
<td>18</td>
<td>92,3</td>
<td>761,5</td>
<td>127</td>
</tr>
<tr>
<td>food waste middle fat</td>
<td>15,6</td>
<td>86,6</td>
<td>681,4</td>
<td>92</td>
</tr>
<tr>
<td>bakery waste</td>
<td>87,7</td>
<td>97,1</td>
<td>764</td>
<td>650</td>
</tr>
<tr>
<td>stale bread</td>
<td>65</td>
<td>97,2</td>
<td>763</td>
<td>482</td>
</tr>
<tr>
<td>Cheese waste</td>
<td>79,3</td>
<td>94</td>
<td>904</td>
<td>674</td>
</tr>
<tr>
<td>Vegetables</td>
<td>15</td>
<td>76</td>
<td>500</td>
<td>57</td>
</tr>
<tr>
<td>curd cheese</td>
<td>21,8</td>
<td>94,9</td>
<td>670,2</td>
<td>139</td>
</tr>
<tr>
<td>Milk</td>
<td>13,5</td>
<td>94,7</td>
<td>899,1</td>
<td>115</td>
</tr>
<tr>
<td>Chip FAT</td>
<td>95</td>
<td>92</td>
<td>1000</td>
<td>874</td>
</tr>
<tr>
<td>Glycerin</td>
<td>100</td>
<td>99,5</td>
<td>850</td>
<td>846</td>
</tr>
<tr>
<td>Rice second flour</td>
<td>90,3</td>
<td>88,5</td>
<td>590</td>
<td>472</td>
</tr>
<tr>
<td>Fruit Mark</td>
<td>22</td>
<td>97</td>
<td>519</td>
<td>111</td>
</tr>
<tr>
<td>First stomach</td>
<td>15</td>
<td>84</td>
<td>480</td>
<td>60</td>
</tr>
<tr>
<td>Corn silage</td>
<td>33</td>
<td>95,8</td>
<td>586</td>
<td>185</td>
</tr>
<tr>
<td>liquid manure pig</td>
<td>6</td>
<td>85</td>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>liquid manure cow</td>
<td>10</td>
<td>85</td>
<td>400</td>
<td>34</td>
</tr>
</tbody>
</table>

Conclusions

For a sustainable management of diminishing natural resources, the private sector of environmental services is playing an ever more important role in supplying raw materials around the globe and in consequence in preventing climate changes. By focusing on our core fields of business, namely water and environmental services, REMONDIS, a 100% family owned company, wishes to use its leading position to further the conservation of natural resources and prevent climate change around the globe. By doing so, our aim is to continue to be the number one partner across the world for companies, municipalities and citizens – a competent, reliable and future-oriented partner that maximizes its customer’s business through its high level of commitment, without ever forgetting the many ecological and social aspects of our work. In the future, organic waste treatment in order to produce fertilizers and green energy will be a very important part of the development of REMONDIS worldwide. Already today, REMONDIS owns more than 100 facilities for biowaste treatment. These facilities alone are able to recycle over 2 millions tons of this material per year. And we are still developing and looking for new partners in order to apply our know-how to the best environmental purposes.

References
[1] www.lfl.bayern.de/ilb/technik/10225/?sel_list=33%2Cb&strsearch=&pos=left
BIOGAS PRODUCTION FROM CROP STALKS THROUGH ANAEROBIC DIGESTION IN CHINA - FROM RESEARCH TO DEMONSTRATION

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ABSTRACT China is one of the largest agricultural countries in the world. Seven hundred million tons of various crop stalks are generated annually. About half of them are being used as feedstocks for animal, fertilizer and/or soil amendment, raw materials for industry such as paper-making etc. The other half remains unused and is normally burnt in open field. This causes serious air pollution, traffic accidents, and fire disaster. On the other hand, crop stalks are kinds of biomass, which can be potentially used as feedstock for anaerobic digestion for biogas production. However, very few attempts have been made to investigate the potential of using these kinds of lignocellulosic materials as feedstocks to produce biogas. The main reason is that crop stalks are rich in lignin, cellulose, and hemicellulose, which are hard to be biodegraded and used by anaerobic microorganisms. These cause lower digestion rate and biogas yield, making them unsuitable for being used in large scale.

Three key technologies need to be developed before lignocellulosic crop stalks can be used for commercial application, which are pre-treatment, specially-designed digester, and optimized anaerobic digestion parameters. The paper presented an overview of the key technology and demonstration projects of biogas production from crop stalks in China. Four chemical, physical, and biological pre-treatment methods, five types of specifically designed digesters, and typical demonstration projects were introduced. The results showed that NaOH was one of the best pre-treatment chemicals, which could increase biogas yield by 27.3%-64.5%while fungus P. florida could increase biogas by 42%-52%, and grinding pretreatment could increase biogas, but not very much. The digestion time of 45-50 days, loading rate of 65 g/L (TS) were found be the best for the digestion of pretreated stalks. Five types of specifically designed digesters developed were completely-stirred reactor, vertical-flow biofilter, horizontal plug-flow reactor, two-phase anaerobic digester, and dry fermentator. These digesters have been applied to 47 demonstration projects in 20 provinces in China. The volumes of the digesters were around 800-1500 m$^3$, which could provide 400-800 m$^3$ biogas/day for villages with residents of 400-800. All the projects were financially supported by the Ministry of Agriculture of China.

Keywords: Crop stalk, Anaerobic digestion, Biogas, Pre-treatment, Digester
OPTIMIZATION OF THE OPERATIONAL PARAMETERS OF A MESOPHILIC TWO-PHASE ANAEROBIC DIGESTER FOR VEGETABLE WASTE DEGRADATION


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ABSTRACT Vegetable wastes which are disposed from centralized food preparation facilities contain high percentage of water and organic fractions. Anaerobic digestion of this kind of waste has been a topic for long time because the anaerobic process converts waste stream into renewable biogas energy. Compared to some of the conventional disposal methods such as landfill, composting and feed production, industrial anaerobic digestion does have many benefits such as bioenergy production, low environmental pollution and almost no odor and leachate emission. However, the engineering applications of vegetable waste digestion were limited by its low organic loading rate (OLR) and long digestion time. Lots of experimental and pilot studies have been conducted to develop a novel process for high rate digestion of vegetable waste. However, most of them used traditional or modified continuous stirring tank reactors (CSTR) with single stage process because of the consideration of initial investment.

In this paper, optimized anaerobic sludge bed reactors (ASBR) were used with a novel two-phase anaerobic process to achieve fast process startup, high OLR and short digestion time. A series of mesophilic (35°C) batch anaerobic trials were firstly conducted to find the optimal food/microorganisms ratio (F/M=3) and initial OLR (OLR=10 g VS L⁻¹) for quick startup of hydrolysis reactor. This experiment suggested that most of the hydrolysis processes could be finished in 4 d. The above key parameters were successfully applied in a two-phase anaerobic system to achieve a quick and stable startup of hydrolysis reactor (HR) which was operated as ASBR before the ultimate CSTR application. The effluent from HR was fed into the methanogenesis reactor (MR) at OLR of 5 g VS L⁻¹ for sufficient conversion of organic fractions. The hydraulic retention times (HRT) of HR and MR were 4 d and 20 d, leading to an overall digestion time of 24 d. The effluent from MR was mixed with new feedstock and fed back into the HR to maintain stable alkalinity and pH. The digestion system discussed in this paper worked well for 80 d, achieving biogas yield of 660±20 mL g VS⁻¹ and methane content of 60±3%. A higher OLR and shorter HRT would be practicable in further studies.

This study proved that mesophilic two-phase processes are applicable for the digestion of vegetable waste at high OLR and short HRT. The optimization of operational parameters and reactors could help the digestion system to be a better choice than traditional single stage system. A pilot system is under construction to get long-term results from the engineering standpoint.

Keywords: Anaerobic digestion, Two-phase digestion, Vegetable waste, Process optimization
25 FULL-SCALE DRANCO ANAEROBIC DIGESTION PLANTS, EXPERIENCES AND OPPORTUNITIES

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ABSTRACT The DRANCO technology was developed by Organic Waste Systems (OWS) in the eighties as one of the first digestion systems for biowaste and municipal solid waste, and OWS has participated in the recent rapid market development. More than 20 years later, DRANCO systems are now used in about 15% of the total installed treatment capacity.

The Brecht facility in Belgium is a very good case study in anaerobic digestion because the plant has now been running for ten years on biowaste. The plant processes about 55,000 tons per year with a very high loading rate and biogas production rate. An average biogas production of 6.8 m³ (240 ft³) biogas per m³ reactor per day (or 6.9 ft³ biogas/ft³ reactor volume) was obtained during the last 8 years.

Another good example of a municipal solid waste plant is the Hille facility in Germany. This plant started up in 2005 and treats about 410 metric tons of the organic fraction of municipal solid waste and 80 metric tons of sludge per week. The average biogas production for the organic fraction of MSW is about 120-125 Nm³ per ton.

Since 2006, the company has also been involved in anaerobic digestion of energy crops, manure and crop residues using the DRANCO-FARM technology. During the initial three years, the facility’s permit allowed only a 500 kW production. In the beginning of 2009, a new permit was issued to produce 1 MW and since then OWS took steps to increase the biogas production in the DRANCO-FARM reactor. Biogas productivity has increased dramatically and electrical output has risen from 500 kW up to 1,000 kW per hour. Currently, OWS is achieving loading rates of 16 to 17 kg VS/m³/d (1 lb VS/ft³/day), about five times the rate of a typical wet digestion system operating at 10% TS and 90% VS/TS.

Keywords: Dry digestion, DRANCO, Biogas
INFLUENCE OF FOOD WASTE LEACHATE ON THE ANAEROBIC GRANULATION PROCESS IN A UASB REACTOR

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ABSTRACT The potential use of food waste leachate on the anaerobic granulation of flocculent sludge in an upflow anaerobic sludge blanket (UASB) reactor was examined for the effective startup of the two-phase anaerobic digestion of food waste. To understand the effects of the granulation process, we conducted two methods of increasing the organic loading rate (OLR): controlling the chemical oxygen demand (COD) concentration (days 1-56) and flow rate (days 57-89). During the first phase (days 1-56), sludge particle size did not increase and remained at 52.6 μm, while sludge volume index (SVI) gradually decreased. In the second phase of the OLR increase (days 57-89), granulation of flocculent sludge was observed and sludge particle diameter abruptly increased to 121.8 μm on day 89 (20.4 kg-COD m⁻³ day⁻¹). However, low COD removal efficiency of 45% was observed under high OLR conditions of 20.4 kg-COD m⁻³ day⁻¹. These results suggest that overloading occurred at the end of experiment, even though the effective granulation of flocculent sludge was observed.

Keywords: UASB, Anaerobic digestion, Food waste leachate, Granulation

Introduction

In the late 1970s, the upflow anaerobic sludge blanket (UASB) process was developed by Lettinga et al. [1]. The UASB reactor has been put into practical use as a popular method for the treatment of low-concentration suspended solids (SS) and medium- to high-strength industrial wastewater. To apply UASB to a wide range of wastewater types, many studies on the anaerobic digestion of high-concentration SS wastewater such as palm oil mill effluent were examined [2].

Recently, the UASB process has also been attempted for anaerobic digestion of municipal solid waste (MSW) containing high-concentration SS [3, 4]. These reactors in the studies consisted of a UASB reactor and an acidogenic reactor. An acidogenic reactor, where the high-concentration SS of MSW could be solubilized and degraded to intermediary products such as volatile fatty acids (VFA), for pretreatment was set up before the UASB reactor. In the process that followed, MSW leachate containing VFA was converted into methane in a UASB reactor. Generally, granules in these experiments are created from synthetic wastewater or collected from working full-scale UASB reactors. However, in the start-up period at a UASB plant, granules must be created from flocculent sludge by using actual wastewater because such granules are in limited supply. Therefore, the feasibility of the granulation process using target wastewater in a UASB reactor should be evaluated from a practical viewpoint.

The aim of this study was to examine the potential use of food waste leachate on the anaerobic granulation of flocculent sludge in an upflow anaerobic sludge blanket (UASB) reactor. Increasing the organic loading rate (OLR) is usually achieved by controlling the COD concentration or flow rate. These two methods of increasing the OLR were also examined to evaluate their effects on the granulation process.

Materials and Methods

Food Waste Leachate and Seed Sludge

Food waste was collected from a cafeteria at Soka University. The food waste was size-reduced with a home disposer while adding tap water, and then solubilized in a solubilization tank under anaerobic conditions over 4 days. SS in the solubilized food waste was removed by centrifugation (4720 G, 10 min). Finally, the COD concentration and pH of the food waste leachate were adjusted with tap water and NaHCO₃. The seed sludge for inoculation was collected from the Hokubu Sludge Treatment Center of Yokohama City, Japan, where sewage sludge had been treated as a substrate in an anaerobic digester. The characteristic of the seed sludge used in the experiment is shown in Table 1.
Table 1. Characteristics of seed sludge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids: TS (% wet weight)</td>
<td>2.53</td>
</tr>
<tr>
<td>Total volatile solids: TVS (% wet weight)</td>
<td>1.71</td>
</tr>
<tr>
<td>TVS/TS (%)</td>
<td>0.676</td>
</tr>
<tr>
<td>Suspended solids (g L⁻¹)</td>
<td>45.1</td>
</tr>
<tr>
<td>Volatile suspended solids (g L⁻¹)</td>
<td>28.4</td>
</tr>
<tr>
<td>Particle diameter (μm)</td>
<td>52.6</td>
</tr>
</tbody>
</table>

**Experimental Setup and Operational Conditions**

The UASB reactor consisted of a PVC glass tube with a total effective volume of 4.9 L, a height of 100 cm, and an inner diameter of 7.9 cm. The UASB reactor was maintained under mesophilic (37 ± 1 °C) conditions and inoculated with 3.5 L of flocculent sludge. The OLR was increased by controlling the COD concentration (2.55 to 7.65 kg-COD m⁻³ day⁻¹) and flow rate (8.16 to 20.4 kg-COD m⁻³ day⁻¹; Table 2).

Table 2. Operation parameters of UASB reactor

<table>
<thead>
<tr>
<th>Influent COD (mg-COD L⁻¹)</th>
<th>Flow rate (L day⁻¹)</th>
<th>OLR (kg-COD m⁻³ day⁻¹)</th>
<th>HRT (day)</th>
<th>Upflow velocity (m day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 38</td>
<td>5000</td>
<td>2.5</td>
<td>2.55</td>
</tr>
<tr>
<td>2</td>
<td>39 48</td>
<td>10000</td>
<td>2.5</td>
<td>5.10</td>
</tr>
<tr>
<td>3</td>
<td>49 56</td>
<td>15000</td>
<td>2.5</td>
<td>7.65</td>
</tr>
<tr>
<td>4</td>
<td>57 67</td>
<td>10000</td>
<td>4.0</td>
<td>8.16</td>
</tr>
<tr>
<td>5</td>
<td>68 74</td>
<td>10000</td>
<td>8.0</td>
<td>16.3</td>
</tr>
<tr>
<td>6</td>
<td>75 89</td>
<td>10000</td>
<td>10</td>
<td>20.4</td>
</tr>
</tbody>
</table>

**Chemical analysis**

Samples of influent and effluent were collected daily from the UASB reactor. COD, pH, VFA, SS, VSS, SVI, biogas composition were measured. Sludge samples from the UASB reactor were taken from all sampling ports before changing the OLR. The particle diameter of the sludge was measured on a particle analyzer.

**Results and Discussion**

**Variation of Sludge Properties**

The diameter of the sludge particles increased after day 68 and granules were observed on day 89 (Fig. 1(A)). Loci of the sludge particle distribution in the UASB reactor were almost the same from day 38 to day 67. Peaks of the loci throughout the first phase of OLR increase (days 1-56, controlled by influent COD) were maintained at 52.6 μm, while SVI gradually decreased from 36.9 to 21.9 mL g⁻¹ SS⁻¹ with the increase of OLR (Fig. 1(B)). In the second phase of OLR increase (days 57-89, controlled by adjusting flow rate) granulation of the flocculent sludge was observed. Sludge particle diameter abruptly increased to 69.6 μm on day 74 and reached 121.8 μm on day 89. Imai et al. [5] reported that in the granulation process using synthetic wastewater, sludge particle diameter abruptly increased as a result of...
high flow rate, while a high COD concentration contributed only slightly to the increase in particle size. The results of the present study suggest that flow rate is also a key parameter in the granulation process with food waste leachate. SVI on Day 74 showed a value similar to a previous experiment that used synthetic wastewater [6]. This research confirmed that functional granules could be formed from flocculent sludge using food waste leachate.

COD removal efficiency remained consistently above 95% up to day 56 (Fig. 2). No VFA accumulation in the effluent was observed up to 8.16 kg-COD m\(^{-3}\) day\(^{-1}\). After day 68, COD removal efficiency was drastically reduced to about 45% on day 89. From day 68, high VFA concentrations of around 2.2 g L\(^{-1}\) were observed and reached a maximum concentration of 5.4 g L\(^{-1}\) by the end of the experiment. VFA concentration is well known to be one of the most practical parameters for accurate control of anaerobic digestion [7]. Although VFA had accumulated in the reactor after day 68 and pH variations did not indicate overloading at the end of experiment as pH values remained around 8 until day 83. These results suggest that VFA concentration could be a reliable indicator for the early detection of process inhibition, as shown in previous studies.

Conclusions

The granulation of flocculent sludge using food waste leachate was conducted for the effective startup of two-phase UASB digestion of food waste. Granulation of flocculent sludge was observed and the sludge particle diameter abruptly increased to 121.8 μm on day 89 (20.4 kg-COD m\(^{-3}\) day\(^{-1}\)). This study confirmed that functional granules could be formed from the flocculent sludge using food waste leachate.

Acknowledgements

This research was made possible by Formation of Center of Excellence for Private University from MEXT (Ministry of Education, Culture, Science and Technology, Japan), 2009-2013. In addition, this study was supported in part by a Grant-in-Aid for Scientific Research Aimed at Establishing a Sound Material-Cycle Society from the Ministry of the Environment, Japan (K2010). We are grateful to Hokubu Sludge Treatment Center, Yokohama, Japan, for the preparation of the seed sludge.

References

ALKALINE PRE-TREATMENT OF PULP AND PAPER MILL SLUDGE FOR ANAEROBIC DIGESTION

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ABSTRACT
This work studied the hydrolysis kinetics and the solubilization of pulp and paper sludge (PPS) under a pH in the alkaline region (11-13), as a pretreatment stage for anaerobic digestion. The hydrolysis rate for solubilization of volatile suspended solids (VSS) followed a first-order rate. A linear hydrolysis model was derived from the experimental results leading to a satisfactory correlation between the hydrolysis rate coefficient and pH. The mean value of the rate constant k for the second phase was 0.52; and the correlation parameter “a” for PPS attained to 3.31. The CODs concentrations in each reactor ranked in the order of A1<A2<A3, as well as the VSS reduction during the hydrolysis process. 50-60% increase of CODs was observed during the first hour and about 70% of VSS was solubilized during the first 3 h. The result indicated that alkali/NaOH pretreatment could be an effective method for improving PPS solubilization for anaerobic digestion.

Keywords: Pulp and paper sludge, Alkaline, Na OH, Pretreatment, Hydrolysis

Introduction
Sludge handling represents 30-40% of the capital cost and about 50% of the operating cost of many wastewater treatment facilities. In the industries with serious pollution, the yield of sludge made from pulp & paper making wastewater was enormous, which was 5-10 times higher than that from the municipal wastewater. In general, 65kg of dry pulp & paper mill sludge (PPS) was produced in the secondary sedimentation tank for 1 t of paper making wastewater treatment. In China, 526×10 4 t of dry PPS was produces in 2007, and 618×10 4 t will produce in 2020 [1]. As PPS contains proteins (22-52%), lignin (20-58%), carbohydrates (0-23%), lipids (2-10%), and cellulose (2-8%) [2], the PPS has to be stabilized sufficiently to reduce its organic content, odor problems, and other contamination before ultimate disposal.

Anaerobic digestion is used as a common method for sludge stabilization leading to an energy recovery bonus in the form of methane gas production. The demands for higher efficiency processes have prompted the need for pretreatment methods in order to improve substrate solubilization and digestibility. Most studies focus on thermal, mechanical, chemical or biological process as a pretreatment stage of sludge and their effect on the methane production. These studies include chemical pretreatment at ambient temperature and alkaline or acidic conditions [3-5], thermal pretreatment in the moderate temperature range [6, 7], mechanical pretreatment [8], biological-microbial enzymes or bacteria pretreatment [9, 10] or their combination [11]. Few studies focus on the hydrolysis kinetics during pretreatment.

The most important parameter for controlling anaerobic digestion is the concentration of bicarbonate alkalinity which has to be as high as possible. The volatile acids produced during digestion can inhibit the methane production due to the fact that the pH can be decreased towards the acidic region. The bicarbonates are in equilibrium with the soluble CO2 producing a strong buffering at neutral pH. Carbon dioxide is a digestion product, so the strength of the buffering depends on the presence of cations. Hence, in many anaerobic digestion cases, it is necessary to add appropriate amounts of alkali in the form of lime or sodium or potassium hydroxide in order to keep the pH in the neutral region [12]. In addition, alkaline treatment of organic material was reported to induce swelling of particulate organic, making the cellular substances more susceptible to enzymatic attack [13]. As a result, the biodegradability of the solid phase may be enhanced significantly.

In this work, pretreatment of PPS at ambient temperature in alkaline conditions, by adding NaOH was examined systematically regarding their effect on PPS solubilization for anaerobic degradation.
Materials and Methods

Methodology

The PPS samples used for the experimental work was obtained from the secondary clarifiers (normally settling tanks) of the Guangzhou Pulp & Paper Plant in China which was usually dewatered to 60-70% moisture content at the end process of waste water treatment. PPS samples were collected prior to each experiment, stored in the refrigerator (0-4°C) immediately and analyzed for total solids (TS), volatile solids (VS), organic carbon (OC), total nitrogen (TN) and pH according to the Standard Methods for the Examination of Water and Wastewater [14]. Total solid suspensions of 10% (w/v) in 40 mL of NaOH solution were prepared by using 20g of the above described stored raw material. The total volatile suspended solids (VSS) content of the sludge used (PPS) was 3.96% (w/v). In order to study the hydrolysis process of the activated sludge, a series of experiments were performed under various temperature and pH values. A total of 3 experimental sets were carried out at ambient temperature (32°C) with pH at 11, 12 and 13, and numbered A1, A2 and A3.

About 10 batch reactors of 125 mL active volume each were used in each set of experiments. The application of 10 batch reactors instead of one had to do with the accuracy of the intermediate results. The batch hydrolysis process took over 10 h and by terminating the process of one reactor every one-hour. Soluble COD and VSS were measured for the total contents of the reactors every hour by terminating one reactor at a time. Duplicates were run for all experimental sets.

Apparatus and Methods of Analysis

The 30 reactors were placed in a shaker with the temperature maintaining at ambient temperature (32°C). Stirring of the reactors by magnetic devices was on a continuous basis. At the beginning, as well as during the course of each experiment, the pH was regulated in order to keep it at the desirable level by adding 40 mL of NaOH solution in an appropriate concentration.

‘‘Standard Methods’’ of analysis [14] was employed to estimate VSS and CODs. The statistical and correlation analysis of the results were carried out utilizing the techniques given in Taylor [15].

Hydrolysis Kinetics

At constant temperature and pH, the rate of hydrolysis is a first-order function for the conversion of particulate biomass to utilizable soluble substrate [16]. In this study a first-order rate expression of the degradable particulate COD, was tested, according to the following expression:

$$\frac{d(COD)}{dt} = k(COD_{p} - COD_{s})$$

(1)

Where, CODs= soluble COD concentration, mg/L; CODp =particulate COD concentration, mg/L; CODnh =nonhydrolyzable CODp concentration, mg/L; COD\(_{\infty}\)=maximum theoretical soluble COD, mg/L=CODp-CODnh; k=first-order hydrolysis rate constant, h\(^{-1}\).

In the above equation, the two unknown parameters, k and COD\(_{\infty}\) can be determined by the method of nonlinear curve fitting of experimental data especially for this type of differential equation described by Thomas [17] and proved by Vlyssides et al. [18]. According to this method the experimental quantities of (t) and (t/CODs\(^{-1}\)) have linear relationship: (t/CODs\(^{-1}\))\(^{1/3}\)=A +B(t). The constants A and B are determined from experimental data using a conventional linear regression method. After this, the COD\(_{\infty}\) and k are estimated according to the following equations: COD\(_{\infty}\)=1/(6A\(^{2}\)B) and k=4.8387B/A.

The correlation between soluble COD production and VSS reduction can be in accordance with Eq. (2) which is derived from Eq. (1) after defining the correlation constant ‘‘a’’.

$$\frac{d(VSS)}{dt} = \frac{1}{a} \frac{d(COD)}{dt} = \frac{k}{a} (COD_{p} - COD_{s})$$

(2)

Where a = correlation parameter = d (COD)/d(VSS)

(3)
The correlation parameter “a” depends on the hydrolyzed material. For hydrocarbons the “a” value is about 1.2, while for proteins and amino acids it is about 2.0 and for fats and lipids 2.5 [18]. So the values obtained for “a” will indicate the type of the hydrolyzed materials.

Results and Discussion

From the experimental results for the dry solids before hydrolysis, the following composition was obtained: OC 32.75 %, VS 62.3 %TS, TN 1.09 %. Experimental data related to CODs and VSS concentrations during hydrolysis process were given in Figs. 1 and 2.

An increase of CODs concentration as well as a decrease of VSS evaluated the hydrolysis process. For the hydrolysis conditions, a rapid increase of CODs was observed during the first hour (Fig. 1). Then a decreasing rate on the CODs production was observed until to the peak value. For more intensive hydrolysis conditions (pH=13), the COD solubilization increased significantly until to the 9th hour of hydrolysis, when about 90% of the solubilization rate had been achieved. At pH=13 and after 9 h of hydrolysis, the CODs concentration was about 15,317 mg/L, obviously increased comparing with the CODs concentration of 9, 809 mg/L after 1 h of hydrolysis. The solubilization rate in reactor A3 (pH=13) was 38.6% and 66.9% higher than those in A2 and A1, respectively.

In Fig. 2 and Fig. 3, the VSS concentration and % VSS reduction were presented. The VSS solubilization during the first 3 h (pH=11 to pH=13) was about 70% of the final value obtained after 10 h of hydrolysis due to the larger easily biodegradable organics (e.g. carbohydrate, starch) existing in the sludge during the first 3 h, instead of the refractory organics (e.g. cellulose, hemicelluloses, lignin) retained in the sludge during the last 7 h. The VSS concentration dropped below 37.2 % of TSS (from an initial value of 39.0 % TSS) after 3 h of hydrolysis in all experimental conditions, with a slightly positive effect of higher alkalinity. Changing the pH value from 11 to 13 during the hydrolysis process could obviously affect VSS by decreasing significantly their concentration, which indicated that the solubilization rate increased with the alkalinity; the VSS reduction rate was still increasing significantly after 9 h of hydrolysis (pH=13) due to the high alkalinity. The VSS concentration in each reactor showed the following trend during the hydrolysis process: A3<A2<A1, contrary to the % VSS reduction trend of A3>A2>A1; that is to say, more % VSS reduction, less VSS concentration retained in the reactor based on the same concentration of initial VSS in each reactor.

For each pH condition, the hydrolysis constant rate k and the maximum theoretical soluble CODs were estimated according to Eq. (1). The good fit of the experimental data to Eq. (1) proved that VSS hydrolysis followed a first-order kinetic model to the remaining nonhydrolyzed COD. These results were presented in Fig. 4 and Table 1, where it was shown that CODs was increased with a pH increase, while the hydrolysis rate constant k was decreased. Especially in the case of pH=13, the calculated values of k appeared to decrease rapidly even though alkalinity was increased.

In Fig. 5, the relation between correlation parameter “a” calculated from equation (3) and the measured COD value was presented. From these results, it could be concluded that there was a relatively good correlation. For CODs concentration less than 16,000 mg/L, the “a” parameter was expressed as: a=0.976 ln(CODs)-6.1778 (R²=0.9013).

The “a” values varied with CODs concentration which increased with the alkalinity. Therefore, for higher pH value, the “a” value was also higher. While the CODs concentration was higher than 15,000 mg/L (pH=13), the “a” parameter almost remained the constant value: a=3.31.
The interest for further hydrolysis was limited because CODs reached concentration of 16,000 mg/L, which was very close to the COD$_{\infty}$ of initial PPS (16,405 mg/L), as well as higher retention hydrolysis time would lead to higher installation cost, because of higher hydrolysis tank volumes.

The maximum of “a” value for PPS (3.31) was higher than hydrocarbon (1.2), proteins (2.0) and fats (2.5) [18]. It indicated that a number of organics in PPS was refractory, which was consistent with the result got by Lin [4]. The “a” value depended on the varieties of the materials; for different hydrolyzed material, the “a” value had the trend: PPS > fats and lipids > proteins and aminoacids > hydrocarbons, which indicated to a certain extent that the process of PPS solubilization started with the hydrolysis of carbohydrates, followed by aminoacids and proteins, and then by fats and lipids, and finally by the refractory organics (e.g. cellulose, hemicellulose, lignin).

![Figure 4. Correlation of (t/COD$_2$)$^{1/3}$ and time](image)

![Figure 5. Correlation factor (a) in relation to CODs](image)

Table 1. The calculation results for the degradation constant of k and theoretical COD$_{\infty}$

<table>
<thead>
<tr>
<th>pH</th>
<th>T/°C</th>
<th>A</th>
<th>B</th>
<th>k b)/h$^{-1}$</th>
<th>COD$_{\infty}$ b)/mg·L</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>32</td>
<td>0.0855</td>
<td>0.0097</td>
<td>0.549</td>
<td>2350.42</td>
<td>0.9394</td>
</tr>
<tr>
<td>12</td>
<td>32</td>
<td>0.0573</td>
<td>0.0064</td>
<td>0.540</td>
<td>7931.57</td>
<td>0.9666</td>
</tr>
<tr>
<td>13</td>
<td>32</td>
<td>0.0467</td>
<td>0.0045</td>
<td>0.466</td>
<td>16982.53</td>
<td>0.9588</td>
</tr>
</tbody>
</table>

Linear analysis for COD$_{\infty}$ and k calculated values led to the following relations: COD$_{\infty}$=-78704+7316.06 pH (R$^2$=0.9816), k=1.02-0.04 pH (R$^2$=0.8303).

Conclusions

CODs concentrations in each reactor improved while the VSS contents decreased during the hydrolysis process. CODs concentrations in each reactor ranked in the order of A1<A2<A3, as well as the VSS reduction. Contrary, the VSS contents in the reactors had the trends of A1>A2>A3.

There were a rapid initial phase of one hour duration time and a subsequent slower phase that followed a first-order kinetic model during hydrolysis. The mean value of k for the second phase was 0.52. In this work, “a” increased with CODs content until to the maximum (3.31).

The results indicated that alkali/NaOH pretreatment could be an effective method for improving PPS solubilization for anaerobic digestion.

References


PERFORMANCE OF VEGETABLE WASTES ANAEROBIC DIGESTION AT DIFFERENT INOCULUMS AND ORGANIC LOADS

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ABSTRACT In order to research the suitability of vegetable wastes for anaerobic digestion, the study was carried out to monitor the effect of organic loads and inoculum on performance of anaerobic digestion of vegetable wastes in single reactor, on the basis of analyzing characteristics change of vegetable waste with season. When the organic feed was increased to 2.0 gVS·l⁻¹·d⁻¹, the biogas production rate can be stable at 3.0 L/d to 3.5 L/d and the methane content was between 55% and 58%. From the relations between COD and methane production, the following can be estimated: When the organic load was 1.75 gVS·l⁻¹·d⁻¹, around 0.348 L methane can be obtained with 1 gCOD removal within the reactor and comparable with the theoretical value of 0.395 L.

Key words: Vegetable waste; Anaerobic digestion; Organic loading, Inoculum ratio

Introduction

A huge amount of vegetable waste were being produced in day to day life and also from the process of agricultural production. Generally, the fresh fruit and vegetable wastes account for 20% to 50% of municipal solid wastes in Asian countries [1]. With the adjustment of industrial structure in rural areas, there will be an increasingly share of vegetable production [2]. The vegetable wastes are always mainly produced in the processes of food processing, handling, transportation and other area in the vegetable market, restaurants, residential areas and etc [3]. Anaerobic digestion of fruit and vegetable wastes features less secondary pollution, production of recyclable clean energy and other advantages [4]. H. Bouallagui et al. [5] used 18-liter anaerobic digester to study hydraulic retention time (HRT) of its anaerobic digestion. They found that it functions well when HRT equals to 20 days and the organic load was 2.8 kg of volatile solids (VS) per cubic metre per day. From the semi-continuous experiment on fruit and vegetable wastes, Rene’ Alvarez and other researchers found that about 0.3 m³·kg⁻¹VS can be produced and methane content will account for about 54–56% when OLR ranged from 0.3 to 1.3 kgVS·m⁻³·d⁻¹ [6].

This article focused on the impact of different Inoculums and organic loading rate (OLR) on methane production of anaerobic digestion.

Materials and methods

Materials

Vegetable wastes collected from school canteen and vegetable leaves, stems and roots were mixed with the ratio of 1:1:1 for the study purpose. Conducive to digestion, the raw wastes had been sized reduced, then chopped to uniform particles and stored at 4°C refrigerators. The literature showed that the optimal C: N: P of vegetable substrate biomass should be 100 to 128:4:1 [10]. No additional nitrogen should be added when the C: N: P of vegetable substrate biomass was close to this range.

Experimental Device

The designed horizontal reactor is adopted for experimental purpose. The reactor is made of plexiglass, with a total volume of 15 L. Horizontal agitator whose mixer shafts were connected with frequency-switch motor and timer, were sealed mechanically and can stir at intervals. The external part of tank is insulated with blankets and insulation materials, and is connected temperature sensor and temperature-control switch so that the digestion temperature can be kept at 35 °C. The baffle is installed at the bottom of the reactor.
Results and Discussion

The Comparison of Inoculum

The inoculums were cow dung, pig manure and anaerobic digestate. Figure 1 shows the biogas potential of vegetable waste and methane output of cow dung, pig manure and anaerobic digestion. In the reaction process of digestive juice, it ranks highest in terms of the average daily methane production and total methane production, reaching 0.5L and 6.5L respectively. The pig manure follows, reaching 0.3 L and 5.2 L respectively. Both of them perform significantly better than that of cow dung. In the initial phase of the experiment, the methane production of digestive juice is slightly less than that of pig manure, featuring slow start. With the operation of the system, the domesticated species group in the microbial digestion features more advantages so that the predominant bacteria under the appropriate temperature and sufficient substrate can grow rapidly.

Figure 1. Comparison of different inoculation methane properties

Figure 2. Comparison of the methane content of different inoculums

Figure 2. indicates the methane content of cow dung and pig manure, anaerobic digestive juices that are coordinated with the vegetable wastes. It also concludes that the rate for digestive juice to produce methane and peak value are two days later than those of pig manure. When the microbial populations in digestive juices are activated and begin breeding, the methane content will be gradually increased. The performance
of cow dung may be the worst for the reason that most of the anaerobes died in open air when it has been exposed to the air a long time. However, the methane production and methane content of cow dung will quickly surpass those of pig manure and maintain stable. It will keep from 30% to 35% at the later time, which is higher than 25% to 30% for pig manure.

On the whole, the digestive juice and pig manure, which can ensure that the system can be started faster and witness more advantageous flora.

Performance of Anaerobic Digestion on Various Organic Load

Methane Production

Figure 3. depicted the daily gas production changes during the process of anaerobic digestion of vegetable waste within the reactor. The daily gas production was very low and was around $0.5 \text{L} \cdot \text{d}^{-1}$ when the initial organic loading rate of $1.5 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$. This may be because the microbes are still in the adaptation phase so that bacteria group synergies between the breeding have not yet reached its best. However, the gas production was gradually increased and stabilized between $2.5 \text{L} \cdot \text{d}^{-1}$ to $3 \text{L} \cdot \text{d}^{-1}$ after one-week of reactor operation. After 15-days with the stable conditions, the organic load was increased up to $1.75 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$ on 27th day and next 48hrs were continuously monitored for the gas production rate, which dropped from $2.65 \text{L} \cdot \text{d}^{-1}$ to $2.40 \text{L} / \text{d}$. It began to increase after a week. The process indicates that gas production fluctuations are not obvious when the anaerobic digestion is stable. On 37th day, the gas production was consistent and stable between $2.8 \text{L} \cdot \text{d}^{-1}$ and $3.4 \text{L} \cdot \text{d}^{-1}$ When the organic load is increased up to $2.0 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$, the gas production was stable and maintained between $3.0 \text{L} \cdot \text{d}^{-1}$ and $3.5 \text{L} \cdot \text{d}^{-1}$.

Figure 3. Daily gas production over time

Figure 4 shows the changes in gas production rate with respect to time. When the organic load rate getting increased from $1.5 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$ to $1.75 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$, the gas production rate in the stable phase has been increased by 3.4%. Therefore, it can be noted that the useable organic matters were increased after materials were added. Anaerobe can break down more substrate and produce more biología. However, the gas production rate was decreased when the load was getting increased to $2.0 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$. The average ratio is decreased by 6.2% compared with $1.5 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$.

The Biodegradable Analysis under Different Organic Load

Table 1 compiled the biodegradability analysis of vegetable waste under different organic load rate. The average daily methane production will be increased with increasing load. However, the actual amount converted methane is lower than the theoretical methane production. When the organic load was $1.75 \text{gVS} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$, around $0.348 \text{L}$ methane can be obtained with 1gCOD removal within the reactor and comparable with the theoretical value of $0.395 \text{L}$.
Figure 4. The changes of gas production rate over time

Table 1. The biodegradability of different organic load

<table>
<thead>
<tr>
<th>Load (gVS•l⁻¹•d⁻¹)</th>
<th>1.50</th>
<th>1.75</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average daily methane production (L•d⁻¹)</td>
<td>1.40</td>
<td>1.70</td>
<td>1.73</td>
</tr>
<tr>
<td>Daily average removed COD (g•d⁻¹)</td>
<td>4.31</td>
<td>4.89</td>
<td>5.04</td>
</tr>
<tr>
<td>Theoretical methane production (L•d⁻¹)</td>
<td>1.70</td>
<td>1.93</td>
<td>1.99</td>
</tr>
<tr>
<td>The actual amount converted methane (L•gCOD⁻¹)</td>
<td>0.325</td>
<td>0.348</td>
<td>0.343</td>
</tr>
</tbody>
</table>

Conclusion

Compared the gas production of anaerobic digestion after the vegetable wastes are inoculated with pig manure, cow dung and digestive juices, we can find that inoculums of fermentation broth and pig manure can ensure faster start-up and produce more dominant bacteria group. In the anaerobe inoculated with digestive juice and pig manure, the gas production will increase as the load increases. When the organic load was increased up to 2.0gVS•l⁻¹•d⁻¹, the gas production was stable i.e., between 3.0 L/d and 3.5 L/d and the methane content ranged between 55% and 58%. From the relationship between COD and methane production, the following can be resulted: When the load is 1.75 gVS•l⁻¹•d⁻¹, 0.348 L methane can be obtained with 1gCOD removal and which is close to the theoretical value of 0.395 L.

References

ANAEROBIC CO-DIGESTION OF VEGETABLE WASTE WITH SPENT YEAST

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ABSTRACT Malaysia generates 19,100 tons/day of solid waste and a total of 68.7% is organic waste. Vegetable solid waste (VSW) from wet market contributes approximately 3.5% of the total waste generation. Spent yeast is one of the solid wastes generated from brewery industry, which is around 2.1 million kg a year at the rate of 2 to 4 kg/hl of beer produced. Objective of this research is to compare co-digestion of vegetable solid waste and a fraction of spent yeast against digestion of vegetable solid waste only. The experiment was carried out in an anaerobic and dark condition at ambient temperature. The organic loading rate (vegetable solid waste to spent yeast ratio), composition of vegetable solid waste and speed of shaker were varied to investigate their effects during the digestion process. The VSW and yeast was reacted in a 100-ml reactor and placed in the shaker during 7-days of experiment. pH of samples was adjusted to 5 in order to suppress methanogenic activity. The TSS (total suspended solids), TDS (total dissolved solids) concentration, volume of biogas and hydrogen content in biogas were determined during the experiment. The result showed negative effect of co-digestion compared to individual digestion of VSW in terms of biogas production, i.e. less biogas was collected than the single digestion of VSW. The pH decreased to the range of 3.5 to 4.5 for all the samples. The hydrogen content in biogas is very low, in range between 0.014 and 0.002% due to the fact that the process has still undergone hydrolysis process and might also the methanogenic process has taken place. The hydrogen yield was 0.886 x 10^-3 ml per ml of sample. It can be concluded that the optimum conditions for this co-digestion process is 200 rpm with organic loading rate of 4:1 as the digestion is higher, in term of TSS and TDS removal. On the other hand, volume of biogas was found higher in experiment at 300 rpm. The composition of VSW does not carry significant effect on the process.

Keywords: Vegetable solid waste, Spent yeast, Co-digestion, Organic loading rate