Stepwise Alkaline/Ultrasound Pre-treatment of Waste Activated Sludge Prior to Anaerobic Digestion

FIELD OF INVENTION

BACKGROUND OF INVENTION

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Cost for sludge treatment and disposal may be as high as 50% of the total operating cost for a wastewater treatment plant. Big organic particulates are separated during the sedimentation process as primary sludge (PS). During the biological treatment process, organic pollutants in wastewater are consumed by microorganisms and converted into carbon dioxide and biomass. Part of the generated biomass is recycled back to the activated sludge tank, while the surplus is separated and becomes waste activated sludge (WAS). Due to their high organic concentrations, PS and WAS should be stabilized so that these materials can be disposed of safely.

Anaerobic digestion is commonly accepted as an ideal method for stabilizing sludge for safe disposal or utilization. It provides the advantages of low biomass yield, high stabilization degree and the production of methane gas. Despite the advantages of anaerobic treatment of sludge, anaerobic stabilization is a time-consuming process. It is widely recognized that hydrolysis limits the rate of an anaerobic digestion process. The anaerobic digestion rate for WAS is considered to be low. WAS mainly consists of intact microorganisms and their secretions. During the activated sludge process, bacterial cells form flocs, the structure of which is enhanced by extracellular polymeric substances (EPS). This complex structure protects microorganism from being degraded and makes the cell lysis and hydrolysis rate much lower.

Ultrasonication has proven to be an effective method for pre-treating WAS. Both extracellular and intracellular substances are solubilized during ultrasonication. After

ultrasonication more organics become available in the liquid phase and this accelerates the subsequent anaerobic digestion.

Cavitation bubbles are formed within the sludge when ultrasound is applied to it. The huge hydro-mechanical shear force caused by the collapse of these cavitation bubbles has been shown to be the predominant sludge disintegration mechanism (Wang et al., 2005). However, the thermal effect and generation of radicals, which had been postulated to also disintegrate sludge, were shown to provide a relatively insignificant contribution compared to the mechanical effect (Wang et al., 2005).

Chiu et al. (1997) demonstrated that higher SCOD concentration could be achieved by combining alkaline pre-treatment and ultrasonication. With the help of a mathematical model, Wang et al. (2005) illustrated that high pH values accelerated the COD solubilization rate during ultrasonication. Kim et al. (2010) quantified the synergistic effect when these two pre-treatment steps were combined. They speculated that the synergistic effect observed was because NaOH made cell walls more vulnerable to ultrasound attack (Kim et al., 2010). In other words, the mechanical mechanism of ultrasound sludge disintegration was improved in the presence of NaOH. They also pointed out that this conclusion was only a speculation, and that there may be other possibilities and more concrete evidence is needed. The above process uses a relatively large amount of NaOH and the need to expend significant amounts of energy due to a long ultrasonication step. Therefore, there remains a need to improve the disintegration of PS and WAS.

SUMMARY OF INVENTION

A novel process has been developed, which involves less NaOH addition and less treatment time (and hence potentially lower energy input requirement), but with higher sludge solubilization and increased methane production.

In a first aspect of the invention, there is provided a process for pre-treating an organic waste, comprising the steps of:

(i) providing an organic waste;

(ii) treating the organic waste with ultrasound and a first dose of an alkaline and/or peroxide composition; and

(iii) adding a second dose of the alkaline and/or peroxide composition after a period of time, while continuing treatment of the waste with ultrasound, wherein

in step (ii) the treatment of the organic waste with ultrasound and the first dose of an alkaline composition are started simultaneously or concomitantly.

In certain embodiments, the ultrasound treatment may have a power density of from 0.5 to 3 W/mL, such as from 0.7 to 2.8 W/mL (e.g. the power density is 1.4 W/mL, 2.8 W/mL or, more particularly, 0.7 W/mL)

In further embodiments, the organic waste may be subjected to treatment with ultrasound for a total time of from 5 minutes to 1 hour, such as from 7 minutes to 18 minutes (e.g. 9 minutes).

In still further embodiments, the organic waste may be subjected to treatment with ultrasound that is conducted at a frequency of from 19 kHz to 200 kHz, such as about 20 kHz.

In yet still further embodiments, the alkaline composition may be lime or a metal hydroxide and the peroxide composition is hydrogen peroxide. For example, the metal hydroxide can be KOH, $Mg(OH)_2$ or, more particularly, NaOH.

In still further embodiments, the alkaline and/or peroxide composition is in a concentration sufficient to provide a concentration of from 0.01M to 0.1M when added to the organic waste, such as from 0.02M to 0.05M (e.g. 0.02 M).

In yet still further embodiments, each dose of the alkaline and/or peroxide composition is from 0.025 g/gTS to 0.5 g/gTS (e.g. each dose of the alkaline and/or peroxide composition is from 0.05 g/gTS to 0.25 g/gTS, such as from 0.1 g/g TS to 0.15 g/g TS). For example, when the alkaline and/or peroxide composition is NaOH, each dose may be from 0.025 g NaOH/ gTS to 0.25 g NaOH/g TS (e.g. from 0.05g NaOH/g TS to 0.15 g NaOH/g TS, such as 0.1g NaOH/g TS).

In yet still further embodiments, the process may further comprise the addition of further doses of the alkaline and/or peroxide composition after a period of time, while continuing treatment of the waste with ultrasound. For example, the period of time is from 2 to 10 minutes (e.g. from 3 to 7 minutes, such as 5 minutes) from the addition of the previous dose of alkaline material.

In still further embodiments, the process may further comprise feeding the pre-treated organic waste into an aerobic or an anaerobic digester. For example, the anaerobic digester may be a mesophilic anaerobic digester or a thermophilic anaerobic digester.

In yet still further embodiments, the organic waste may be one or more selected from the group consisting of a sludge, food waste, oily waste, solid waste with a high organic content and any combination thereof. For example, the sludge may be a waste activated sludge or a primary sludge.

In still further embodiments, the total solids content of the organic waste may be from 0 to 50 g/L.

In a second aspect of the invention, there is provided a waste treatment plant comprising a pre-treatment apparatus that comprises an ultrasonicator apparatus and adapted to work in the process of the first aspect of the invention.

In embodiments of the invention, the plant may further comprise a device to provide two or more doses of an alkaline or peroxide composition separated by a period of time.

In still further embodiments of the invention, the ultrasonicator apparatus may be adapted to act in a batch or continuous fashion.

In yet still further embodiments of the invention, the waste treatment plant is a wastewater treatment plant or a sludge treatment plant.

FIGURES

Figure 1: COD solubilization caused by alkaline addition.

Figure 2: Evolution of SCOD, protein and carbohydrate concentration during ultrasonication.

Figure 3: Change of median diameter during ultrasonication.

Figure 4: 3-D demonstration of synergistic effect at different combination of ultrasonication time and NaOH dosage.

Figure 5: Comparison of conventional alkaline treatment and novel stepwise alkaline treatment (orange curve).

Figure 6: Influence of power density on combined alkaline/ultrasound treatment.

Figure 7: BMP curves for ultrasound, alkaline, combined ultrasound/alkaline and novel step wise alkaline addition/ultrasound pre-treatments.

DESCRIPTION

Disclosed herein is a process for the pre-treatment of organic waste, said process comprising the steps of:

(i) providing an organic waste;

(ii) treating the organic waste with ultrasound and a first dose of an alkaline and/or peroxide composition; and

(iii) adding a second dose of the alkaline and/or peroxide composition after a period of time, while continuing treatment of the waste with ultrasound, wherein

in step (ii) the treatment of the organic waste with ultrasound and the first dose of an alkaline composition are started simultaneously or concomitantly.

When used herein, the term "organic waste" relates to organic materials in a liquid medium that may comprise biodegradable solids. Examples of organic wastes include, but are not limited to a sludge, food waste, oily waste, solid waste with a high organic content or any combination thereof. It will be appreciated that the sludge may be a waste activated sludge or a primary sludge.

As noted above, the process relies upon the use of ultrasound and chemical treatment in a simultaneous manner in order to achieve a synergistic effect. In this context, it should be noted that the addition of the first dose of the chemical agent (i.e. the alkaline and/or peroxide composition) may be before, at the same time as, or after the initialisation of

ultrasound treatment and *vice versa*, provided that the treatments overlap (i.e. the treatments are simultaneous or concomitant).

When used in the current process, the ultrasound treatment may have a power density of from 0.5 to 3 W/mL (e.g. one can use a power density of from 0.7 to 2.8 W/mL, such as any one of 0.7 W/mL, 1.4 W/mL and 2.8 W/mL). It is preferred to use a power density of 0.7 W/mL.

As noted above, while at least one additional dose of the alkaline and/or peroxide composition is needed, the ultrasound treatment continues uninterrupted when said additional dose is added. Therefore, in the current process, the organic waste may be subjected to (continuous) treatment with ultrasound for a total time of from 5 minutes to 1 hour (e.g. from 7 minutes to 18 minutes, such as 9 minutes).

In order to achieve good results, it has been found that the use of ultrasound at a frequency of from 19 kHz to 200 kHz (e.g. about 20 kHz) is optimal.

While the alkaline composition may be any alkaline material, specific alkaline materials that may be mentioned herein include lime or a metal hydroxide (e.g. KOH, $Mg(OH)_2$ or, more preferably, NaOH) or any combination thereof. When used herein, "lime" refers to $CaCO_3$, CaO, Ca(OH), or any combination thereof.

Alternatively or additionally, the process may use a peroxide composition instead. Examples of peroxide compositions include, but are not limited to, hydrogen peroxide.

It will be appreciated that the alkaline and/or peroxide compositions are added in at least a first dose and a second dose, though further doses are contemplated in the process. Each dose of the alkaline and/or peroxide composition is intended to provide a synergistic effect in combination with the use of the ultrasound treatment. In certain embodiments, the alkaline and/or peroxide composition is in a concentration sufficient to provide a concentration of from 0.01M to 0.1M of the alkaline and/or peroxide material when added to the organic waste. For example, the resulting concentration may be from 0.02M to 0.05M, such as 0.02 M. It will be understood, that the actual dose used for the

first, second and subsequent doses may be the same or different (e.g. the first dose may be larger than the second dose and the second dose larger than a third dose etc).

Alternatively or additionally, each dose of the alkaline and/or peroxide composition may be determined with regard to the weight of the composition compared to the amount of total solids in the waste. A suitable range for each dose would be from 0.025 g/gTS to 0.5 g/gTS (e.g. from 0.05 g/gTS to 0.25 g/gTS, such as from 0.1 g/g TS to 0.15 g/g TS). For example, when the alkaline and/or peroxide composition is NaOH, each dose may be from 0.025 g NaOH/ gTS to 0.25 g NaOH/g TS (e.g. from 0.05g NaOH/g TS to 0.15 g NaOH/g TS, such as 0.1g NaOH/g TS). As above, the actual dose used for the first, second and subsequent doses may be the same or different.

The current process separates the doses of the alkaline and/or peroxide composition by a period of time, while continuing treatment of the waste with ultrasound. The exact period of time between each dose and the subsequent dose will vary depending on the type of organic waste (or combination thereof) being treated. The period of time may be determined based upon a levelling off of in the level of COD (e.g. SCOD), or any similar measurement that enables one to determine when the alkaline and/or peroxide composition has essentially been entirely consumed by chemical reaction with the waste. In most cases, the period of time may be from 2 to 10 minutes from the addition of the previous dose of the alkaline and/or peroxide composition, such as from 3 to 7 minutes (e.g. about 5 minutes). This dosage strategy can be thought of as pulsatile dosing of the organic waste with an alkaline and/or peroxide composition while the organic waste is being subjected to treatment with ultrasound.

It will be appreciated that an organic waste subjected to the current process will be ideally suited to further downstream processing, such as the processing provided in an aerobic or an anaerobic digester. Therefore, the current process may also include feeding the pre-treated organic waste into an aerobic or an anaerobic digester. This is a central advantage of the current process, as it not only increases the solubilisation, but also improves the biodegradability of the waste, thereby enabling a better processing of the waste under aerobic and/or anaerobic digestion. Any type of anaerobic or aerobic digestion may be undertaken. Types of anaerobic digestion processes that may be

mentioned include those using a mesophilic anaerobic digester or a thermophilic anaerobic digester.

It will be appreciated that the current process may be used with a wide range of organic wastes. For example, the total solids content of the organic waste used in the current process may be from 0 to 50 g/L.

The current process may be used at any conceivable scale from a laboratory bench, through the industrial treatment of organic waste. As such, there is also provided a waste treatment plant comprising a pre-treatment apparatus that comprises an ultrasonicator apparatus and adapted to work in the process as described hereinbefore.

The plant may be further adapted to comprise a device to provide two or more doses of an alkaline or peroxide composition separated by a period of time. In addition, the ultrasonicator apparatus may be adapted to act in a batch or continuous fashion.

In addition, the current plant may be a wastewater treatment plant or a sludge treatment plant.

It will be appreciated that the process described herein will have particular application where there is interest in the treatment of wastewater with energy reduction and recovery, and where there are constraints on disposal of such waste (e.g. sludges). Energy recovery is of growing importance given the growing awareness of the energy-environment nexus. Current state-of-the-art wastewater treatment processes have a significant carbon footprint and the process disclosed above may help to reduce said energy footprint. The process and apparatus used therein can be used in both sewage and industrial wastewater treatment plants, and can be used in new plants or as a retrofit addition to existing facilities. In the retrofit scenario, the addition of the apparatus for running the disclosed process can also serve to expand the treatment capacity of the existing facility and hence avoiding the need for the reconstruction of existing treatment facilities as needs increase.

EXAMPLES

Materials and Methods

Sludge Samples

Mixtures of primary sludge and thickened waste activated sludge (a ratio around 1:1 based on dry solids) were collected from a municipal water reclamation plant for the study. Properties of the sludge are listed in Table 1. The anaerobic sludge was collected from the anaerobic digester at the water reclamation plant, which was operated in CSTR mode and at hydraulic retention time (HRT) of 28days. Anaerobic sludge was incubated at 35°C for one week to consume residual organics before it was used as inoculum.

Parameter	Value range
Total solids (g/L)	16.2-17.2
Volatile solids (g/L)	12.6-13.4
Total suspended solids (g/L)	15.5-15.9
Volatile suspended solids (g/L)	12.4-13.0
Total COD (mg/L)	19,500-25,000
Soluble COD (mg/L)	700-1,200
Soluble Protein	<100
Soluble Carbohydrate	<50

Table 1

Analytical methods

pH was measured with a pH meter (Agilent, model 3200P) with an accuracy of 0.01. Buffer solutions of pH 4, pH 7 and pH 10 (Fisher, UK) were used to calibrate the pH meter each time before use.

The Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Soluble Chemical Oxygen Demand (SCOD) and Total Chemical Oxygen Demand (TCOD) were measured as described in Standard Methods

(APHA, 1999). The coefficient of variations (CoV) for ten identical samples were 2.7%, 3.8%, 2.8%, 4.8%, 1.9% and 1.6% respectively.

Protein concentration was determined with Lowry's method (1951) using bovine serum albumin (Sigma-Aldrich) as standard and a UV spectrophotometer (Shimadzu, UV-1800) against the blank at a wavelength of 750 nm. The coefficient of variance was within 2.8% for 10 identical samples. As the precise chemical formula of the proteins detected was not determined, the percentage of soluble COD represented by protein had to be estimated by assuming a stoichiometric conversion factor of 1.5 which is derived from the typical formula of proteins ($C_{16}H_{24}O_5N_4$) presented in Rittmann and McCarty (2001).

Carbohydrate concentration was determined with the sulfuric-phenol method (DuBois et al., 1956) using D-Glucose (Merck, Germany) as standard. To convert into COD, 1g carbohydrates, assumed as $C_6H_{12}O_6$, is equivalent 1.07 g COD (Rittman and McCarty, 2001). The coefficient of variance was within 6.8% for ten identical samples.

Particle size distribution was measured with a particle size analyzer (Shimadzu, model SALD-3101) and based on laser diffraction. It provided information on median diameter, mean diameter, and the percentages of particles within defined diameter ranges.

Sludge disintegration degree (DD_{COD}) was used to express the ratio of solubilized COD to the maximum possible COD solubilization and was used to quantify the sensitivities of different sludge to ultrasound attack (Muller et al., 1998):

$$DD_{COD} = \frac{SCOD_T - SCOD_O}{SCOD_{NaOH} - SCOD_O}$$

Where $SCOD_T$ is the Soluble COD of treated sample, $SCOD_{NaOH}$ is the Soluble COD of sample immersed in 1M NaOH (ratio 1:1) at 90°C for 10 minutes and $SCOD_O$ is the soluble COD of the raw sample.

NaOH

Sodium Hydroxide (Merck, Germany) was first made into a 3M stock solution. Different NaOH dosages were achieved by adding a different volume of stock solution into a sludge sample. NaOH pre-treatment concentrations in this experiment were set to 0.01M, 0.02M, 0.05M and 0.1M which corresponded to NaOH dosages of 0.025gNaOH/gTS, 0.05gNaOH/gTS, 0.125gNaOH/gTS and 0.25gNaOH/gTS. After the addition of NaOH, the vessel was shaken for a predetermined time manually.

Ultrasonication Conditions

Ultrasonicator (Misonix, Q700) with a frequency of 20 kHz and a maximum power input of 700W was used in this experiment. A solid tip probe #4208 with a diameter of 19.1mm was installed and its maximum applicable amplitude was 60 μm. 80% of the maximum amplitude was used and the corresponding power input was around 140W. Power density is the power received per millilitre of sludge (W/mL). Treated sludge volume was 200 mL for most of the experiments. 50 mL and 100 mL sludge samples were also tested to create different power densities. Power Ultrasonication energy input was quantified with both specific energy input (SEI) and ultrasonication time, the SEI was calculated as follows:

$$\mathrm{SEI} = \frac{\text{Total energy input (J)}}{\text{Total solids in sample (g)}} = \frac{\mathrm{P} * \mathrm{t}}{\mathrm{V_{sludge}} * \mathrm{TS}}$$

Where P is Power input of ultrasonicator (W), t is the time of ultrasonication (s), V_{sludge} is Volume of treated sludge (L) and TS is the Total solids concentration of treated sludge (g/L). During ultrasonication the temperature was monitored and refrigerated below 30°C with an ice-water mixture if necessary.

Anaerobic Biodegradability

A Biochemical methane potential (BMP) assay was conducted according to Owens et al. (1979) in 120 mL serum bottles to quantify the anaerobic degradability of WAS samples. For the BMP assays, 10 mL of substrate (raw and treated WAS), 30 mL of degassed

inoculum (VS: 0.99 g/L) and 30 mL biomedium were added to serum bottles. Sludge samples treated with NaOH were neutralized by the addition of 0.1M HCl drop-wise until the pH reached around 7.5 prior to the anaerobic digestion tests. A mixture of 20% CO_2 and 80% N_2 was used to purge each bottle for three minutes to create an absolute anaerobic environment. All bottles were incubated in an orbital shaker at 35°C. The biogas volumes were regularly measured using a wetted glass syringe and reported at atmospheric pressure and a temperature of 20°C. The composition of biogas was determined using gas chromatography (Agilent, 7890A GC systems), with a thermal conductivity detector (TCD). Two blanks containing the inoculum and the biomedium were run in parallel, and the methane produced was subtracted from the methane produced in the bottles containing the samples.

Example 1

Preliminary Test on the Effect of NaOH Alone

The alkaline treatment time was normally longer than 30 minutes in past results (Kim et al., 2010, Li et al., 2012). In this experiment, the maximum NaOH pre-treatment time was set to be only 9 minutes. As shown in Figure 1, the reaction between NaOH and sludge is a fast process. For a NaOH dosage that is higher than 0.02 M, significant solubilization of COD was observed after the first minute of NaOH addition. A slight increase of SCOD followed in the second minute and thereafter the SCOD concentration became relatively stable. However, for a NaOH dosage of 0.02 M, only a slight increase of COD was observed, and for a NaOH dosage of 0.01 M, almost no increase of SCOD was observed. This suggested that even though NaOH is a highly reactive and corrosive reagent, 0.02 M is recommended as the lowest effective dosage threshold.

Protein and carbohydrate concentrations were also tested. The sludge treated for five-minutes was selected as representative and the protein and carbohydrate concentrations were measured. The soluble protein concentrations were 2,120 mg/L, 1,490 mg/L, 320 mg/L and less than 50 mg/L for NaOH concentrations of 0.1M, 0.05M, 0.02M and 0.01M, respectively. Most of the solubilized substances after alkaline treatment were proteins. Taking the NaOH dosage of 0.1M as an example, the soluble protein concentration increase was around 2,000 mg/L which was equivalent to 3,000 mg/L COD according to the conversion coefficient mentioned above in the materials and

methods section. This is quite substantial compared to the SCOD increase caused by alkaline treatment, which was around 3,500 mg/L.

Example 2

Preliminary Tests on the Effects of Ultrasound (ULS) alone

The maximum ultrasonication time used here was set to 9 minutes, in order to keep consistency with the alkaline pre-treatment of Example 1. According to Khanal et al. (2007), ultrasonication efficiency will decrease after a certain time because of the exhaustion of easily disrupted substances around cavitation bubbles. The optimum treatment time is normally chosen before the efficiency drop. As shown in Figure 2, COD solubilization kinetics did not change with increasing time. This indicated that a treatment time less than nine minutes made good use of the ultrasonic energy and would give satisfactory performance.

The solubilized protein and carbohydrate concentration were converted to their equivalent COD concentrations, as described in the materials and methods section above. For example, after three minutes, the soluble protein concentration increased from 60 mg/L to 500 mg/L. The difference (440 mg/L) is equivalent to 660 mg/L COD, which represented around 50% of the COD solubilized during the same period. Similarly, 14% of COD solubilization was due to carbohydrates. As the ultrasonication time increased, the percentage of equivalent COD of ultrasound induced protein solubilization increased to 70%. This indicated in the first three minutes ultrasound caused damage to floc structure and solubilized extracellular biopolymers which contained both protein and carbohydrate. This is confirmed by significant median particle size drop in the first three minutes as shown in Figure 3. As protein is the principle composition of cells (Kim et al., 2010), with the increasing ultrasonication time, intracellular substances which contained relatively high protein concentration were released and increased the protein percentage as a component of the solubilized substances. This conclusion was also supported by past results which have shown ultrasound caused obvious extracellular substances solubilization prior to severe cell lysis (Lehne et al., 2001, Wang et al., 2006). Nevertheless, compared to NaOH treatment ultrasonication treatment obviously showed a poorer performance in protein solubilization but better performance in floc disruption.

In terms of disintegration degree, only 32% disintegration degree could be reached after nine minutes of ultrasonication.

Example 3

Combined Alkali and Ultrasound Pre-Treatment

In order to investigate the influence of sequence on this combined treatment, different sequences (i.e. ULS-NaOH, NaOH-ULS and simultaneous treatments) were compared. Simultaneous treatment as well as NaOH-ULS caused more COD solubilization than ULS-NaOH treatment. Past results also supported that simultaneous combination NaOH and ultrasound was the best combination sequence (Jin et al., 2009). The following experiments were therefore conducted with simultaneous NaOH/ULS treatment.

A NaOH dosage of 0.05M was selected to evaluate the performance of combined alkaline and ultrasonication pre-treatment. As shown in Table 2, combined treatment showed more volatile solids destruction and higher sludge disintegration than individual ultrasonic or alkaline pre-treatment. DD of combined treatment reached around 80%, which exceeds the maximum possible DD of 50% induced by mechanical pre-treatment (Lehne et al., 2001). This indicated that some of the mechanically hardly disintegrable substances in sludge were solubilized in the presence of chemicals. Apart from the high disintegration degree, the combined pre-treatment has also the advantages of size reduction which cannot be achieved by chemical pre-treatment.

	Median Diameter (μm)	TSS reduction (%)	VSS reduction (%)	Disintegration degree (%)
Raw	42.3	0	0	0
ALK (0.05M)	42.7	9.6	7.9	19.7
ULS (9min)	12.1	10.9	10.3	31.7
ALK (0.05M)+ULS (9min)	14.2	24.2	21.8	79.4

Table 2

As shown in Table 2, the DD caused by combined treatment was obviously higher than the sum of ALK and ULS pre-treatment individually. This suggested combination of alkaline and ultrasonic treatment had a synergistic effect on sludge disintegration (in terms of COD).

Example 4

Synergy between NaOH and ULS

The solubilized COD caused by combined treatment consists of three parts: solubilized COD caused by NaOH treatment alone; solubilized COD caused by ULS alone; and solubilized COD caused by the synergistic effect. In order to investigate the influence of the sequence on this combined treatment, different sequences (i.e. ULS-NaOH, NaOH-ULS and simultaneously) were tested with a NaOH concentration of 0.02M. Simultaneous treatment, as well as NaOH-ULS treatment, solubilized almost the same COD (~4100mg/L) and these sequences were more effective than ULS-NaOH treatment (~3600mg/L). This indicated that a better performance was achieved when ultrasonication was conducted in the presence of NaOH. The following experiments were therefore conducted with simultaneous NaOH/ULS treatment.

Synergistic effects at different NaOH dosage and ultrasonication times are shown in Figure 4. This represents the additional SCOD that could be gained by the combination compared to the two treatments applied separately. The synergistic effect increased quickly in the first two minutes, but no obvious change was observed after five minutes. This indicated that addition of NaOH accelerated the subsequent ultrasonication in the first minutes, but the increase of the synergistic effect would be negligible after five minutes.

The synergistic effect was also NaOH concentration dependent. The synergistic COD solubilization caused by 0.02M, 0.05M and 0.1M were similar (~3,500mg/L SCOD), but the synergistic effect caused by 0.01M NaOH (~2,000mg/L SCOD) was obviously lower than the other three dosages. This shows that 0.02M NaOH was enough to cause the optimum synergistic effect, further increase of NaOH concentration did not increase the synergistic COD solubilization. For NaOH concentration lower than 0.02M, less synergistic effect was produced when less NaOH was used. Despite that, the synergistic

SCOD increase caused by 0.01M NaOH and ultrasonication still approached 2,000 mg/L, which was significant.

If Kim and Co-workers' (2010) speculation that "after alkaline addition microorganism cells become more vulnerable for ultrasound attack" is true, then one would expect that more synergistic SCOD should be released at higher alkaline dosages. This is because for alkaline treatment alone, the higher the alkaline dosage is, the more SCOD will be solubilized and more damage will be imposed on sludge. Even though no SCOD increase was observed after 0.01M NaOH addition, considerable synergistic effect was achieved. These results suggested that, in addition to Kim and coworkers' (2010) hypothesis, another synergistic principle must exist that has not been exploited yet. This mechanism functions even at low NaOH dosage (e.g. 0.01M NaOH) and becomes stable when NaOH concentration was at or greater than 0.02M.

Without wishing to be bound by theory, we believe that the presence of NaOH promotes the chemical effect of ultrasound (i.e. hydroxyl radical generation) and causes more COD solubilization. In other words, the presence of NaOH has a "pseudo-catalytic" effect for hydroxyl radicals generation during ultrasonication. During the first two minutes of alkaline addition, because there is a sufficient amount of alkaline ions present, the "pseudo-catalytic" effect was obvious and led to significant synergistic COD release. However, as the chemical reaction between NaOH and sludge proceeded the synergistic effect became insignificant due to lack of "catalyst". This is because the radical's generation is a result of cavitation bubbles formation (Hua and Hoffmann, 1997). When the alkaline concentration is too low, there will not be enough alkaline ions in the vicinity of the cavitation bubbles to promote radicals generation.

Example 5

Step-Wise Addition of NaOH

Based on our hypothesis, as discussed in Example 4, the conventional ultrasound/alkaline treatment was modified to a combination of stepwise alkaline addition and ultrasound treatment to exploit the synergistic effect. In this case, the minimum NaOH dosage needed to reach the best synergistic effect was 0.02M, the amount of NaOH for each addition was set to be 0.02M. The second batch of alkaline

was added after five minutes of ultrasonication, as this was when the synergistic COD solubilization of the first batch stopped increasing. The optimized results are shown in Figure 5.

It is clear from Figure 5 that this novel two-step addition of alkaline/ultrasound treatment was more effective than conventional alkaline/ultrasound treatment. The solubilized COD for this novel treatment was slightly higher than achieved in the conventional combined treatment, whereas the amount of NaOH was only 80% of the amount used in the conventional treatment. The TSS and VSS reduction are 23.2% and 22.6%, respectively, which are similar to the conventional combined pre-treatment. These results confirmed that the second addition of alkaline material was able to produce better, or similar performance, with 20% less NaOH addition. Without wishing to be bound by theory, it is believed that the "pseudo-catalytic" effect recurred due to the re-addition or "pulsed addition" of the alkaline "catalyst".

The influence of power density on this treatment process was also investigated and the results are shown in Figure 6. High power density produces more cavitation bubbles in a specific volume of sludge (Li et al., 2009). When no alkaline material was added, the performance of different power densities did not show any obvious difference for the same specific energy input. Similar results were observed for NaOH concentration of 0.02M. However, when NaOH concentration was 0.05M, more COD was solubilized at higher power densities. When NaOH dosage was low, even more cavitation bubbles exist in a specific volume of sludge at high power density, but the amount of NaOH in the specific volume of sludge was not sufficient to produce more radicals. When NaOH dosage was high, more cavitation bubbles were accompanied with sufficient NaOH in the specific volume of sludge. Thus, when enough "catalyst" was available, radical generation occurred which led to more COD solubilization.

Example 6

Anaerobic Biodegradability

A biochemical methane potential (BMP) assay was used to test the biodegradability change of sludge after various pre-treatments processes.

- Ultrasound pre-treatment with nine minutes and 18 minutes ultrasonication time were tested to evaluate the influence of pure mechanical treatment on methane production.
- 0.05M NaOH treatment was tested to determine the influence of pure chemical treatment on methane production.
- Combined ultrasound/Alkaline treatments were tested to investigate the synergistic effect on methane production. Both conventional (0.05M+ultrasound) and novel stepwise treatment (0.02M+Ultrasound+0.02M+ultrasound) were tested.

The sludge characteristics after each treatment and their corresponding biodegradability are listed in Table 3. This compares the sludge after ultrasound treatment, NaOH treatment and combined ultrasound/alkaline treatment (TS=17.2g/L).

Sample	**SCOD (mg/L)**	**Biodegradability ($mLCH_4/gCOD_{added}$)**
Raw	780	130
9 min ULS	4900	156
18min ULS	6900	161
0.05M NaOH	3200	132
0.05M NaOH+9min ULS	9100	171
0.04M NaOH (stepwise)+ 9min ULS	9300	183

Table 3

The BMP curves for the aforementioned treatment conditions are shown in Figure 7. For all the pre-treated sludges, the methane production achieved in the first four days was much higher than raw sludge. This is because more organics are available in soluble form after alkaline treatment. However, afterwards methane production from alkaline treated sludge was much lower than raw sludge and no anaerobic biodegradability increase was noticed. This indicated that particulate matters became less biodegradable after alkaline treatment especially when said particles remained in big sizes. Such a gas

production decrease was not observed when alkaline treatment was combined with ultrasound. It is suggested that after ultrasonication, the particulate organics are dispersed into smaller fragments that are more readily accessible to enzymatic attack.

Nine minutes of ultrasonication caused a SCOD increase (~4,000mg/L) and the anaerobic degradability of sludge was improved by 20%. 2,000mg/L more COD was solubilized when the ultrasound time was doubled to 18 minutes. However, unlike reported past results that sludge biodegradability was proportional to SCOD concentration after ultrasonication (Grönroos et al., 2005), sludge anaerobic degradability only increased to 24% which was not substantial compared to the 20% increase after nine minutes ultrasonication. This suggested there may be a technical threshold for ultrasonication performance. At the beginning of ultrasonication, mechanical shear force caused solubilization of some hardly degraded organic particulates and made them more readily usable for subsequent anaerobic digestion. However, with the increase of ultrasonication time, some of the solubilized substances are relatively resistant to anaerobic digestion, therefore the sludge biodegradability increase slowed.

With the presence of NaOH, the performance threshold of ultrasound in improving anaerobic digestion was broken. This is because chemical characteristics of some recalcitrant substances were changed under chemical attack. The conventional combined ultrasound/alkaline showed a 31% increase of anaerobic biodegradability, whereas a 40% increase was observed after the novel stepwise combined ultrasound/alkaline treatment.

The combined ultrasound and stepwise alkaline addition treatment led to more methane production than conventional combined treatment. Without wishing to be bound by theory, one possibility is that the second addition of NaOH caused a more synergistic effect and led to more COD solubilization. More organics became available for methanogens. Another possibility is stepwise alkaline addition accelerated radical generation by ultrasound as speculated, and some recalcitrant compounds may be decomposed into smaller readily degradable compounds. To sum up, combined ultrasound and stepwise alkaline addition treatment was proven to be a feasible alternative treatment method for conventional combined ultrasound/alkaline treatment.

Conclusions

A synergistic effect was observed when alkaline treatment was coupled with ultrasound treatment. This synergistic effect can be initiated at NaOH concentration as low as 0.01M. However, NaOH concentration of 0.02M was the minimum concentration needed to achieve the maximum synergistic COD solubilization. Further increase of NaOH concentration increased only COD solubilization but did not increase the synergistic effect. Although high COD solubilization was observed after alkaline treatment, no obvious increase in biodegradability was noticed. Although anaerobic biodegradability was improved after ultrasonication, longer treatment time did not lead to obvious methane production increase. 20% and 24% increase of methane production was observed after nine minutes and 18 minutes ultrasound pre-treatment respectively. Combined alkaline and ultrasound pre-treatment (0.05M+9min ULS) significantly increased anaerobic biodegradability of sludge by 31%. Besides, by modifying the conventional combined treatment into a stepwise alkaline addition/ultrasound combined treatment, 20% NaOH could be saved to achieve the 9% higher methane production (raw sample as the baseline) than conventional combined treatment.

Advantages and improvements over existing methods, devices or materials.
We are proposing a novel process whereby:

1. There is a synergistic effect of NaOH and ultrasonication on SCOD.
2. The combined treatment has improved volatile solids destruction (22 %) and higher sludge disintegration than ultrasonic (10%) or alkaline (8%) pre-treatment applied singly. The TSS removal of the combined treatment was 24%.
3. Stepwise (or pulsed) addition of NaOH resulted in improved performance compared to one single addition at the beginning of the ultrasound treatment.
4. The stepwise addition of NaOH allows for less chemicals to be used (-20%) and more methane to be produced (+9%) compared to other combinations of ULS and NaOH pretreatment.
5. The production of methane in the anaerobic digester increases by about 40% compared to digestion of non-pre-treated WAS.

6. The method developed was using sewage sludge as an example, but it can be applied on other wastes, e.g. (other organic wastes such as food waste and agro-industrial wastewaters such as POME).

The invention discloses a process of pre-treating waste activated sludge (WAS) prior to anaerobic treatment of wastewater. The pre-treatment process according to this invention modifies the conventional combined alkaline addition-ultrasound pretreatment into a stepwise alkaline addition (e.g. NaOH) during ultrasound pre-treatment.

Changes in the Soluble Chemical Oxygen Demand (SCOD) caused by the combined pre-treatment could be due to three sub-processes: SCOD caused by NaOH alone, SCOD caused by ultrasound (ultrasonication) alone, and SCOD caused by the synergistic effect of both acting in concert.

According to this invention, it was noted that the synergistic effect increased rapidly in the first two minutes after the first NaOH addition, but there was no further significant change after five minutes. This indicated that addition of NaOH accelerated the impact of ultrasonication in the first minutes but the chemical components causing the acceleration appear to have been "consumed" thereafter. For improved performance of this invention, the preferred NaOH concentration needed to reach the best synergistic effect is 0.02M. The next dose of NaOH would be added after the first five minutes of ultrasonication or after the increase in COD solubilisation following the first NaOH pulse has levelled off. Such stepwise (or pulsed) addition of NaOH resulted in improved performance compared to the single addition of NaOH at the beginning of the conventional ultrasound treatment method.

The conventional combined single alkaline addition-ultrasound pretreatment showed a 31% increase in anaerobic biodegradability, whereas a 40% increase was observed with this invention's stepwise alkaline addition-ultrasound pretreatment. In addition, the stepwise addition of NaOH allows for lower chemical consumption - 20% NaOH can be saved, while achieving 9% higher methane production.

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CLAIMS

1. A process for pre-treating an organic waste, comprising the steps of:

(i) providing an organic waste;

(ii) treating the organic waste with ultrasound and a first dose of an alkaline and/or peroxide composition; and

(iii) adding a second dose of the alkaline and/or peroxide composition after a period of time, while continuing treatment of the waste with ultrasound, wherein

in step (ii) the treatment of the organic waste with ultrasound and the first dose of an alkaline composition are started simultaneously or concomitantly, wherein the alkaline and/or peroxide composition is in a concentration sufficient to provide a concentration of from 0.01M to 0.1M of the alkaline and/or peroxide composition when added to the organic waste.

2. The process of Claim 1, wherein the ultrasound treatment has a power density of from 0.5 to 3 W/mL.

3. The process of Claim 2, wherein the ultrasound treatment has a power density of from 0.7 to 2.8 W/mL.

4. The process of Claim 3, wherein the power density is 0.7 W/mL, 1.4 W/mL or 2.8 W/mL.

5. The process of Claim 4, wherein the ultrasound treatment has a power density of 0.7 W/mL.

6. The process of any preceding claim, wherein the organic waste is subjected to treatment with ultrasound for a total time of from 5 minutes to 1 hour.

7. The process of Claim 6, wherein the organic waste is subjected to treatment with ultrasound for a total time of from 7 minutes to 18 minutes.

8. The process of Claim 7, wherein the organic waste is subjected to treatment with ultrasound for a total time of 9 minutes.

9. The process of any preceding claim, wherein the organic waste is subjected to treatment with ultrasound that is conducted at a frequency of from 19 kHz to 200 kHz.

10. The process of Claim 9, wherein the organic waste is subjected to treatment with ultrasound that is conducted at a frequency of about 20 kHz.

11. The process of any preceding claim, wherein the alkaline composition is lime or a metal hydroxide and the peroxide composition is hydrogen peroxide.

12. The process of Claim 11, wherein the metal hydroxide is KOH, $Mg(OH)_2$ or NaOH.

13. The process of Claim 12, wherein the metal hydroxide is NaOH.

14. The process of any preceding claim, wherein the alkaline and/or peroxide composition is in a concentration sufficient to provide a concentration of from 0.02M to 0.05M of the alkaline and/or peroxide composition when added to the organic waste.

15. The process of Claim 14, wherein the alkaline and/or peroxide composition is in a concentration sufficient to provide a concentration of 0.02M of the alkaline and/or peroxide composition when added to the organic waste.

16. The process of any preceding claim, wherein each dose of the alkaline and/or peroxide composition is from 0.025 g/gTS to 0.5 g/gTS.

17. The process of Claim 16, wherein each dose of the alkaline and/or peroxide composition is from 0.05 g/gTS to 0.25 g/gTS.

18. The process of any preceding claim, wherein the process further comprises the addition of further doses of the alkaline composition after a period of time, while continuing treatment of the waste with ultrasound.

19. The process of any preceding claim, wherein the period of time is from 2 to 10 minutes from the addition of the previous dose of alkaline material.

20. The process of Claim 19, wherein the period of time is from 3 to 7 minutes from the addition of the previous dose of alkaline material.

21. The process of Claim 20, wherein the period of time is about 5 minutes from the addition of the previous dose of alkaline material.

22. The process of any preceding claim, wherein the process further comprises feeding the pre-treated organic waste into an aerobic or an anaerobic digester.

23. The process of Claim 22, wherein the anaerobic digester is a mesophilic anaerobic digester or a thermophilic anaerobic digester.

24. The process of any preceding claim, wherein the organic waste is one or more selected from the group consisting of a sludge, food waste, oily waste, solid waste with a high organic content and any combination thereof.

25. The process of Claim 24, wherein the sludge is a waste activated sludge or a primary sludge.

26. The process of any preceding claim, wherein the total solids content of the organic waste is from 0 to 50 g/L.