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Optimizing the Synergistic Effect of sodium hydroxide/Ultrasound Pre-treatment of sludge

Xinbo Tian[a] , Wun Jern Ng[a] and Antoine P. Trzcinski[b*]

[a] Advanced Environmental Biotechnology Centre (AEBC), Nanyang Environment and Water Research Institute (NEWRI), Nanyang Technological University, 1 Cleantech Loop, CleanTech One, #06-10, Singapore 637141.

[b] University of Southern Queensland, School of Civil Engineering & Surveying, Faculty of Health, Engineering and Sciences, 4350 Australia

*Corresponding author.

Email: antoine.trzcinski@usq.edu.au

Tel: +61 7 4631 1617

Abstract

Ultrasound (ULS), sodium hydroxide (NaOH) and combined ultrasound/NaOH pre-treatment were applied to pre-treat waste activated sludge and improve the subsequent anaerobic digestion. Synergistic effect was observed when NaOH treatment was coupled with ultrasound treatment. The highest synergistic Chemical Oxygen Demand (COD) solubilization was observed when 0.02M NaOH was combined with five minutes ultrasonication: an extra 3,000 mg/L was achieved on top of the NaOH (1,975 mg/L) and ultrasonication (2,900 mg/L) treatment alone. Further increase of NaOH dosage increased Soluble Chemical Oxygen Demand (SCOD), but did not increase the synergistic effect. Nine minutes and 18 minutes ultrasonication led to 20% and 24% increase of methane production, respectively; Whereas, 0.05M NaOH pre-treatment did not improve the sludge biodegradability. Combined ultrasound/NaOH (9min+0.05M) showed 31% increase of methane production. A stepwise NaOH addition/ultrasound pre-treatment (0.02M+ULS for 5 min + 0.02M+ULS for 4 min) was tested and resulted in 40% increase of methane production using 20% less chemicals.

Keywords: Waste Activated Sludge (WAS); ultrasonication; NaOH; pre-treatment; anaerobic biodegradability.

1. Introduction

In modern wastewater treatment plant, some of the main energy consuming steps are the treatment of excess activated sludge and its final disposal which sometimes account for

half of the operating expenditure of the plant [1]. Organic particles in raw sewage are separated during the sedimentation process as primary sludge (PS). During biological treatment, dissolved organic pollutants in wastewater are metabolized by bacteria into carbon dioxide and biomass. Some of the generated biomass is recycled back to activated sludge tank and the surplus biomass are separated and become waste activated sludge (WAS). Due to their high organic concentration, PS and WAS should be stabilized before disposal.

Anaerobic digestion is widely applied to stabilize the sludge while producing energy in the form of biogas [2]. The main advantages and benefits of the technology include reduction in volumes, low biomass yield, high stabilization degree as well as production of methane gas [3]. Despite the advantages of anaerobic treatment of sludge, anaerobic stabilization is a time-consuming process due to long residence times of typically 30 days in digesters [4]. From a chemical engineering point of view, the conversion rate is rather low with typically 30 to 40% volatile solids conversion to biogas. It is widely recognized that hydrolysis is the slowest step which justifies the long residence times required [5, 6]. The anaerobic digestion rate for WAS is considered to be rather low [7]. WAS consisted of flocs made of bacteria adhering to one another by secreting extracellular polymeric substances (EPS) which enhance the structural integrity of the flocs. The cell walls themselves are also hard to hydrolyze due to glycan strands which limits the rate and extent of hydrolysis [8].

Ultrasonication has been proven to be an effective method to pre-treat WAS. Both extracellular and intracellular substances are solubilized during ultrasonication [9]. After ultrasonication more organics become available in liquid phase and accelerate and improve the subsequent anaerobic digestion [10].

Thousands of cavitation bubbles are formed in the vicinity of bioflocs when ultrasound is applied to sludge. Huge localised pressure caused by the rapid collapse of these cavitation bubbles is proven to be predominant sludge disintegration mechanism [11]. Thermal effect and generation of radicals may also disintegrate sludge but these were proven to be relatively insignificant compared to the hydro-mechanical forces [11]. Dong et al. [12] applied alkali and ultrasound treatment of corn stalk and achieved 57% increase in biogas production together with 71.4% and 77.1% decrease in total and volatile solids, respectively.

Ruiz-Hernando et al. [8] compared NaOH, thermal and ultrasound pre-treatments and the optimum conditions were as follows: 27kJ/g TS for ultrasound, 80°C during 15 minutes for thermal and 157 g NaOH/kg TS for the alkali. The alkali pretreatment exhibited the greatest methane production increase (34%), followed by the ultrasonication (13%), whereas the thermal pre-treatment presented a methane potential similar to the untreated sludge.

Chiu et al. [13] found that combining alkaline pre-treatment and ultrasonication resulted in higher soluble chemical oxygen demand concentrations. Nathan et al. reported that the combined treatment solubilized solids and COD by a factor of 3 to 14. However, the biogas production in batch anaerobic tests was not significantly higher, although the

production rate was enhanced. Tian et al. [15] found that soluble chemical oxygen demand (SCOD) increased from 1200 to 11,000 mg/L after such treatment and that organics with molecular weight around 5.6 kDa were solubilized because of the synergistic effect of ultrasound and alkali. Furthermore, organics with molecular weight larger than 300 kDa increased from 7.8% to 42.3% after NaOH and ultrasonication treatment. Using a mathematical model, Wang et al. [11] found that high pH values (8 to 12) accelerates COD solubilization rate during ultrasonication. Kim et al. [14] quantified the synergistic effect when these two pre-treatments were combined. They speculated that NaOH makes cell walls more vulnerable for ultrasound attack [14]. In other words, the mechanical mechanism of ultrasound sludge disintegration was improved in the presence of NaOH. This was only a speculation and there may be other possibilities and therefore, more concrete evidence are needed. Ultrasonication is already applied at full scale, but the operating costs is sometimes a deterrent. Synergistic effect between NaOH and ultrasound would translate in better results that the sum of results from each technology applied alone. This has therefore the potential to achieve better results using less ultrasound energy and deserves therefore more research.

In this paper, the mechanism of this synergic effect is further investigated and the process is further optimized. A novel method is developed which involves less NaOH addition, shorter treatment time, but higher sludge solubilization and methane production compared to the conventional NaOH/ultrasonication pre-treatment.

2. *Materials and methods*

2.1. Waste activated sludge samples

The sludge was collected from Ulu Pandan wastewater reclamation plant in Singapore where primary and thickened secondary sludge are mixed before the anaerobic digesters [15]. Table 1 lists the relevant characteristics of the sludge. The anaerobic inoculum was taken from a full scale anaerobic digester in the same plant. Anaerobic sludge was incubated at 35°C for one week to consume residual organics before it was used as inoculum.

Table 1. Properties of sludge.

Parameter	Units	Value range
TS	g/L	16.2-17.2
VS	g/L	12.6-13.4
TSS	g/L	15.5-15.9
VSS	g/L	12.4-13
Total COD (mg/L)	mg/L	19,500-25,000
Soluble COD (mg/L)	mg/L	700-1,200
Soluble Protein	mg/L	<100
Soluble Carbohydrate	mg/L	<50

2.1. Analytical methods

Sludge samples were characterized for pH, 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) in triplicates according to standard methods [16]. A 0.45 micron filter was used to obtain the soluble fraction of COD or soluble COD (SCOD). Proteins and carbohydrates concentrations were determined as reported previously [17, 18]. Protein and carbohydrates concentration was

converted to COD equivalent by multiplying by 1.5 and 1.07, respectively [19]. Soluble substances were analyzed in the filtrate after filtration through a 0.45 microns membrane. The particle size distribution of sludge samples before and after pre-treatment was determined by laser diffraction using a Shimadzu particle size analyzer, model SALD-3101. It provided information of median diameter, mean diameter, and the percentage of a certain diameter range possessed. The sludge disintegration degree (DD_{COD}) following the pre-treatments was calculated as previously reported [20]:

$$DD = (SCOD_T - SCOD_0) / (SCOD_{NaOH} - SCOD_0) \times 100\%$$

Where, $SCOD_T$ is the soluble chemical oxygen demand (SCOD) of treated sample, $SCOD_{NaOH}$ is the SCOD of sample measured after immersion in 1 mol/L NaOH (1:1, *V/V*) at 90°C for 10 min (≈12,900 mg/L in this study) and $SCOD_0$ is the SCOD of the untreated sample.

2.2. NaOH pre-treatment

NaOH pre-treatment was carried out using sodium Hydroxide pellets (Merck, Germany) dissolved to obtain the following concentrations: 0.01M, 0.02M, 0.05M and 0.1M, equivalent to the following dosages respectively: 0.025, 0.05, 0.125 and 0.25 g NaOH/g TS. Mixing was carried out at 200 rpm during and after NaOH addition.

2.3. Ultrasonication pre-treatment

The sludge (200 mL) was sonicated using a 20 kHz ultrasonicator (Misonix, Q700). Sonication took place for up to 18 minutes at 80% amplitude with a 19.1 titanium probe.

The power density is the power received per milliliter of sludge (W/mL). Different sludge volumes (50 and 100 mL) were also tested to create different power densities. The ultrasonication time was used to calculate the specific energy input (SEI) as described in [21]. The SEI normalizes the influence of different TS concentration and ultrasonication power density. Sludge samples were kept on ice to prevent overheating above 30°C.

2.4. Anaerobic biodegradability

The anaerobic biodegradability was assessed using the biochemical methane potential (BMP) assay as described previously [22]. Ten mL of substrate (raw or treated sludge), 30 mL of degassed inoculum (VS: 0.99g/L) and 30 mL biomedium were added to 120 mL serum bottles and the biogas composition was determined as previously reported [23].

3. Results and discussion

3.1. Preliminary results of individual NaOH pre-treatment

Sodium Hydroxide (NaOH) treatment time normally was longer than 30 minutes in previous studies [14, 24]. In this experiment, the maximum NaOH pre-treatment time was only set to be nine minutes to achieve a fast process. As shown in Figure 1, reaction between NaOH and sludge is a fast process. The pH in sludge increased from 6.5 to 7.8, 9.7, 12.2 and 12.8 at concentrations of 0.01, 0.02, 0.05 and 0.1M. SCOD concentrations reached 1,350, 1,700, 3,390 and 4,830 mg/L after 9 minutes, corresponding to a disintegration degree (DD) 0.8%, 4.0%, 19.7% and 32.8%, respectively. The calculation for 32.8% is given here as example: DD = 100% x (4,830-900)/(12,900-900) = 32.8%.

This is in line with previous studies where DD of 7.6%, 12.3%, 17.1%, 21.4% and 27% were obtained at pH 9, 10, 11, 12 and 13, respectively by mixing at 200 rpm for one hour [14]. However, in this study, similar results were obtained after 9 minutes of mixing.

At NaOH concentration greater than 0.05M, the high DD was the consequence of cell lysis due to high pH (pH >12.2). This creates a hypertonic environment whereby microbial cells lose their integrity due to the resulting turgor pressure [25]. At NaOH concentrations lower than 0.02M (pH 9.7), the disintegration was insignificant with a DD of 4% which can be explained by the de-agglomeration of some biological flocs due to the alkaline pH [26, 27]. This de-agglomeration can result in smaller flocs and the release of soluble materials which would be reflected by an increase in SCOD, and consequently in an increase in DD.

At NaOH dosage of 0.02M, only a slight increase in SCOD concentration was observed and for NaOH dosage of 0.01M, almost no increase of SCOD was observed. At NaOH dosage higher than 0.02M, a 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. This suggested that even though NaOH is a highly reactive and corrosive reagent, 0.02M is recommended as the lowest effective dosage threshold.

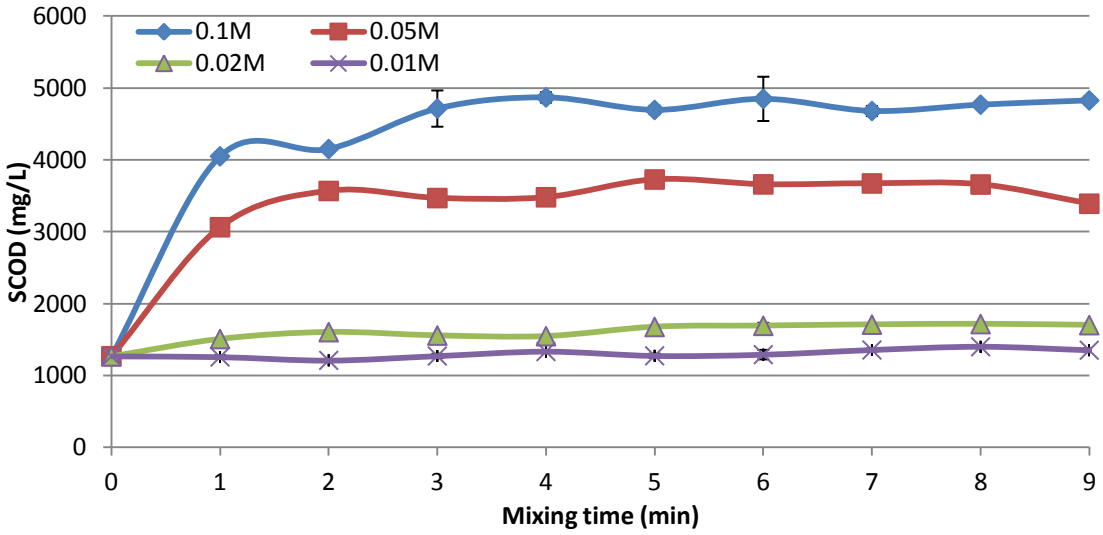


Figure 1. Chemical Oxygen Demand (COD) solubilization caused by sodium Hydroxide (NaOH) addition. The error bars represent the standard deviation associated with triplicate measurements. (TS=17.2g/L).

As no obvious increase of SCOD could be determined after 2 minutes, a sample was taken after five minutes and the proteins concentration were measured. The soluble protein concentration increased by less than 50 mg/L, 320 mg/L, 1490 mg/L and 2120 mg/L, at NaOH concentration of 0.01M, 0.02M, 0.05M and 0.1M, respectively. Most of the solubilized substances after NaOH treatment were proteins. Taking the NaOH concentration of 0.1M as an example, the soluble proteins concentration increased by approximately 2000 mg/L or 3,000 mg/L COD equivalent. This was significant compared to the total SCOD increase caused by NaOH treatment which was around 3,500 mg/L.

3.2. Preliminary results of individual ultrasonication (ULS) pre-treatment

Maximum ultrasonication time was also set to be nine minutes to compare with NaOH pre-treatment. According to Khanal et al. [28], ultrasonication efficiency will decrease after a certain time, because of exhaustion of easily disrupted substances around cavitation bubbles. Optimum treatment time is normally chosen before the efficiency drop.

As it can be seen in Figure 2, the SCOD concentration increased linearly indicating considerable disintegration in the sludge even at low specific energy input. The SCOD reached 4,670 mg/L corresponding to a disintegration degree of 31.7% after 9 minutes or 21 kJ/g TS ULS pre-treatment. This is consistent with [14] who obtained DD of 30.1 and 41.1% at ultrasonication SEI of 15 and 30 kJ/g TS, respectively. As shown in Figure 2, the COD solubilization rate did not change with increasing time. This indicates that less than nine minutes treatment time makes good use of the ultrasonic energy and gives satisfying performance.

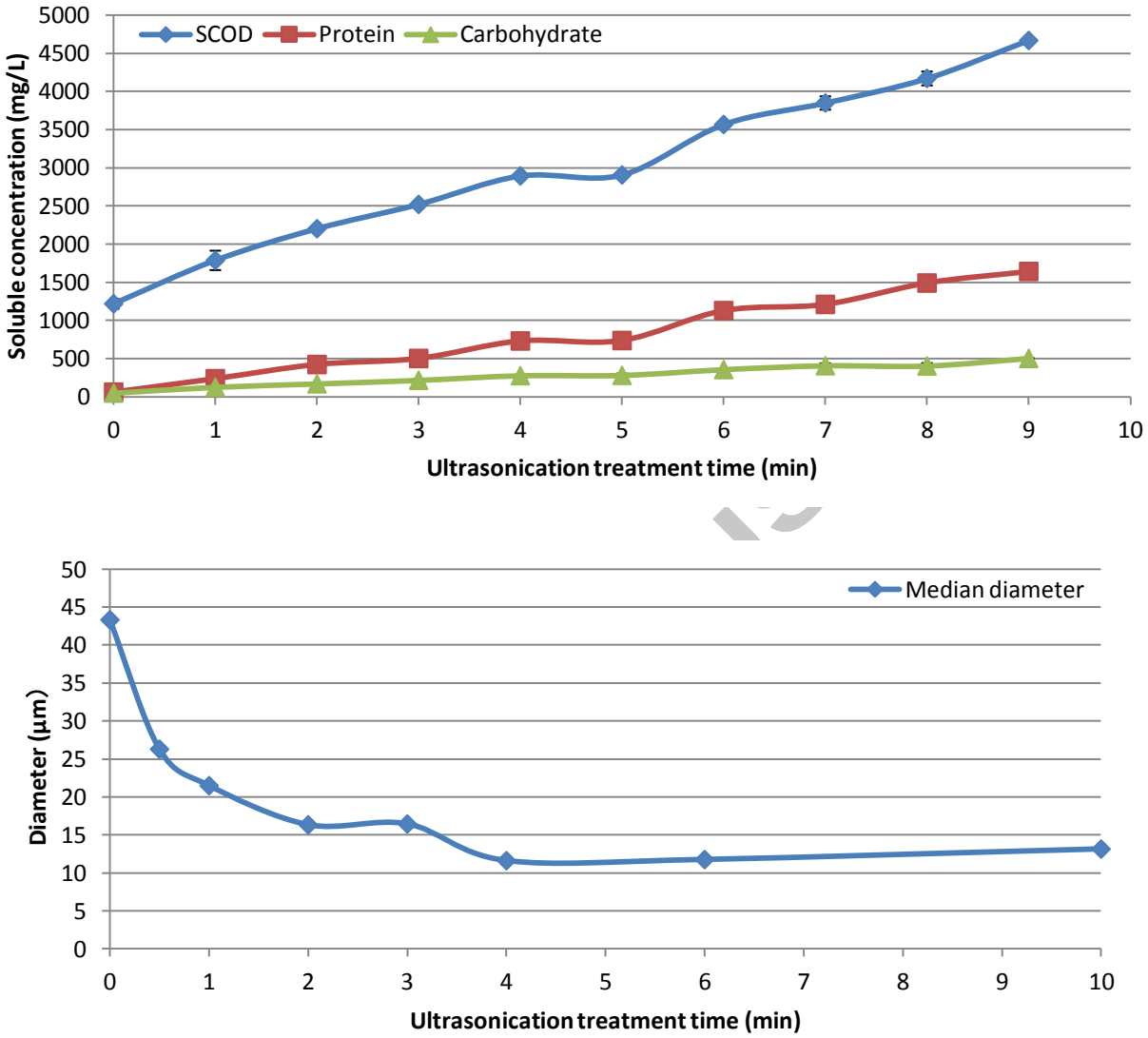


Figure 2. (top)SCOD, soluble protein and carbohydrate concentration during ultrasonication. (Bottom) Change of median diameter during ultrasonication. The error bars represent the standard deviation associated with triplicate measurements. (TS=17.2g/L)

After conversion to COD equivalents, soluble proteins contributed to a significant part of SCOD. For instance, after three minutes the soluble protein concentration increased from

60 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 (660/(2520-1218)x100% = 50.7%). The solubilized carbohydrate represented around 14% of the solubilized COD regardless of the ultrasonication time. As ultrasonication time increased, the percentage of equivalent COD of ultrasound induced by protein solubilization increased to 70% (100% x (1640-50)x1.5/(4670-1220)). This indicates in the first three minutes ultrasound caused damage to floc structure and solubilized extracellular biopolymers which contain both proteins and carbohydrates. This was confirmed by a significant drop in median particle size during the first three minutes as shown in Figure 2 (bottom). As proteins represent one of the major component of cells [19], intracellular substances which contained relatively high protein concentration were released due to ultrasonication, and increased the protein percentage in solubilized substances. This conclusion was also supported by past results which showed that ultrasound caused obvious extracellular substances solubilization prior to severe cell lysis [29, 30]. Nevertheless, compared to NaOH treatment ultrasonication treatment showed a slower performance in terms of COD solubilisation, but better performance in flocs disruption as shown by the rapid decrease in median diameter of flocs.

In terms of disintegration degree (DD), only 31.7% disintegration degree could be reached after nine minutes of ultrasonication. Lehne et al. [29] pointed out that ultrasound pre-treatment is effective in reducing floc size and cause cell lysis. However, some particulate organics can only be chemically solubilized but are relatively reluctant to

mechanical attack [29]. This suggests a combined treatment NaOH/ultrasound could overcome this barrier.

3.3. Combined NaOH and ultrasound pre-treatment

So far, only one study supported that simultaneous combination of NaOH and ultrasound was the best combination sequence among the possible sequences (i.e. ultrasound treatment followed by NaOH addition (ULS-NaOH), NaOH addition with mixing to reach a certain pH or dosage followed by ultrasound treatment (NaOH-ULS) or simultaneous addition of NaOH and ultrasound treatment) [31]. Most previous investigation applied first alkali to the desired pH with mixing for a certain period and then applied ultrasound (NaOH-ULS) [14, 21]. In the present study, at a NaOH dosage of 0.02M, the simultaneous treatment as well as NaOH-ULS treatment solubilized almost the same COD (~4,100 mg/L) which was more effective than the ULS-NaOH treatment (~3,600 mg/L). This clearly shows that the chemical or pH enhanced the effect of ultrasound. 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 NaOH and ultrasonication pre-treatment. As shown in Table 2, the combined treatment resulted in greater volatile solids solubilization and higher sludge disintegration than individual ultrasonic or NaOH pre-treatments. The DD of combined treatment reached almost 80% which exceeds the maximum possible DD of 50% induced by mechanical pre-treatment [29]. To the best of the authors' knowledge, such high DD has not been reported before

and it is believed to be due to the simultaneous actions of NaOH and ultrasound, while past studies applied a sequential treatment. These findings indicate that some of the mechanically hardly disintegrable substances in sludge were solubilized in the presence of chemicals. Apart from high disintegration degree, the combined pre-treatment also has the advantages of size reduction which could not be achieved by chemical pre-treatment. Sahinkaya and Sevimli [32] hypothesized that ultrasonic waves solubilized macromolecules which were then degraded by hydroxyl ions. Such reactions are for instance lipids saponification and proteins hydrolysis by the alkali.

Table 2. Comparison of combined pre-treatment and individual pre-treatment.

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

As shown in Table 2, the DD resulting from the simultaneous treatment reached 79.4% which is more than the sum of NaOH (19.7%) and ULS (31.7%) pre-treatment individually. The highest DD of 79.4% is greater than the maximum DD of 69.4% reported by Kim et al. [14] at pH 13 (reached with a dosage of 0.268 M KOH) for 1 hour followed by 15 kJ/g TS. This suggests that NaOH and ultrasonic provide synergistic effect in terms of sludge disintegration (in terms of COD). The actual synergistic DD was calculated as 79.4 – (19.7+31.7) = 28% which is significantly higher than the maximum synergistic DD of 18.9% reported by Kim et al. [14] for an alkaline treatment at pH 12 (reached with a dosage of 0.133 M KOH) combined with an ultrasonic treatment at 7.5 kJ/g TS (Table 3). Greater synergistic DD could not be reached at ultrasonic treatment of

15 and 30 kJ/g TS. It is interesting to note that alkali and ultrasound were applied in sequence in previous studies [14, 21], whereas our results suggest that the simultaneous treatment is better in terms of SCOD, actual DD and synergistic DD.

Table 3. Synergetic disintegration resulting from combined alkaline and ultrasound pre-treatment in previous studies. DD = disintegration degree.

Reference	Alkaline treatment		Ultrasound treatment		Sequence	Actual DD (%)	Synergistic DD (%)
	Conditions	DD (%)	Conditions (kJ/g TS)	DD (%)			
This study	0.02M NaOH 0.05M NaOH 0.1M NaOH	4 19.7 32.8	21 (9min)	31.7	Simultaneous (9 min)	- 79.4 -	- 28 -
[14]	0.268M KOH pH 13, 1 hour	27	15	30.1	Alkaline-ULS	69.4	12.3
[14]	0.133M KOH pH 12, 1 hour	21.4	7.5	19.5	Alkaline-ULS	59.8	18.9
[14]	0.086M KOH pH 11, 1 hour	17.1	15	30.1	Alkaline-ULS	63.8	16.6
[14]	0.086M KOH pH 11, 1 hour	17.1	30	41.1	Alkaline-ULS	66	7.8
[31]	0.5M NaOH 30min	~30	15	~23	Simultaneous (30 min)	~60	~7
[33]	pH 12, NaOH	-	56.25 (30 min)	~31	Alkaline-ULS	~42	-

3.4. Synergistic effect between NaOH and ultrasound

Synergistic COD solubilization at different NaOH dosages and ultrasonication time are shown in Figure 3 (top). The figure shows the additional SCOD compared to the sum of SCOD obtained from individual treatment applied separately (provided in Figure 1 and Figure 2 top). It is interesting to notice that synergic effect increased quite fast in the first

two minutes, but no obvious change was observed after five minutes. This indicates that the addition of NaOH accelerated the ultrasonication in the first minutes.

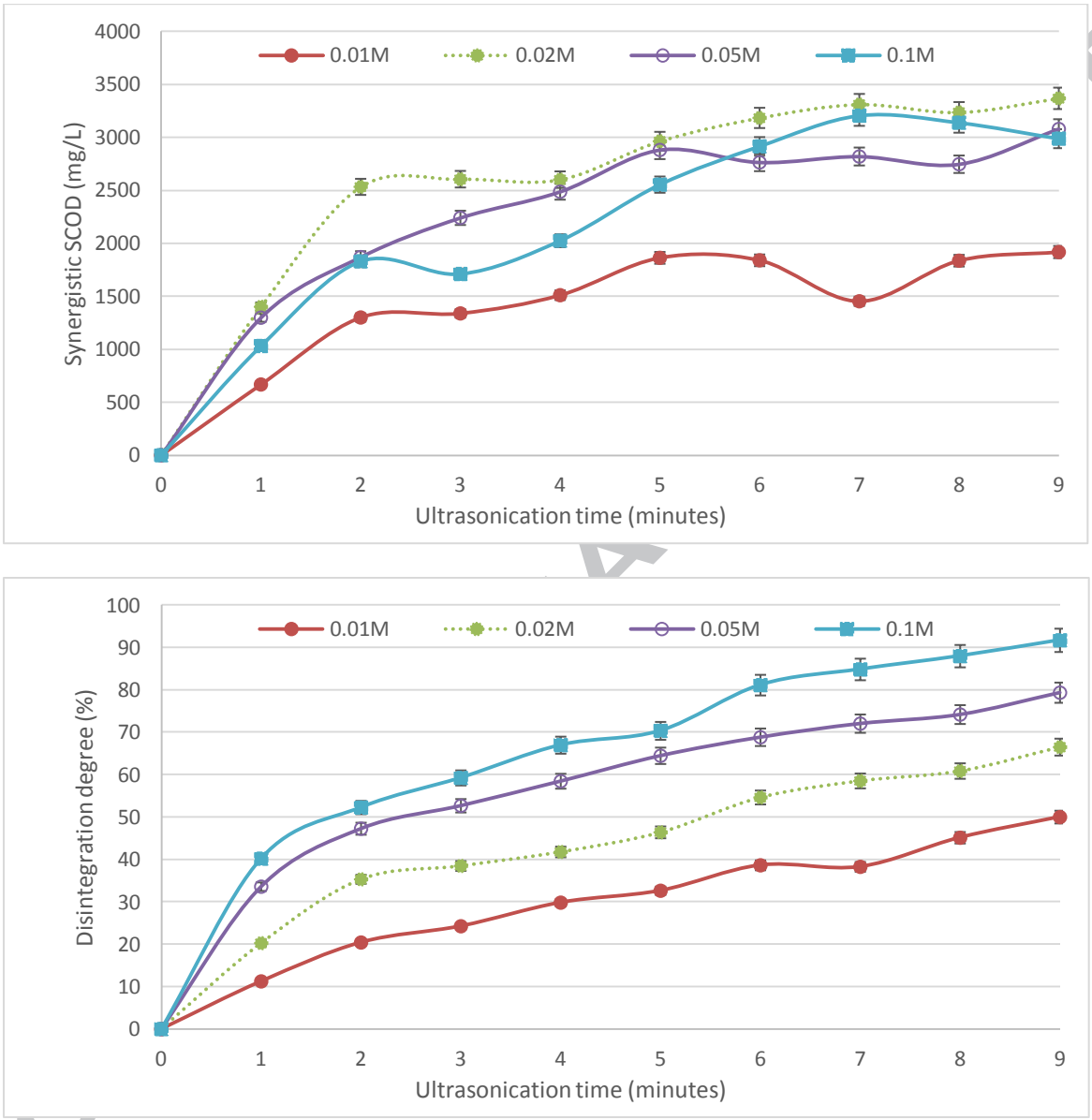


Figure 3. (top) Synergistic SCOD under different combinations of NaOH dosage and ultrasonication time. (Bottom) Disintegration degree under different combinations of NaOH dosage and ultrasonication time. The error bars represent the standard deviation associated with triplicate measurements. (TS=17.2 g/L)

This synergistic effect was also NaOH concentration dependent. The synergistic COD solubilization caused by 0.02M, 0.05M and 0.1M were similar (~3,000 mg/L SCOD), but the synergic effect caused by 0.01M NaOH (~2,000mg/L SCOD) was lower than the other three dosages. This shows that 0.02M NaOH is sufficient to cause the optimum synergistic effect, and higher NaOH concentration did not increase the synergistic COD solubilization. In spite of that, synergic SCOD increase caused by 0.01M NaOH and ultrasonication still approached 2,000 mg/L, which is quite considerable. The corresponding DD are provided in Figure 3 (bottom) where it can be seen that the final DD were 50%, 66%, 79.4% and 91.7% at NaOH dosage of 0.01M, 0.02M, 0.05M and 0.1M, respectively.

According to Kim and co-workers' [14], after NaOH addition microorganism cells become more vulnerable to ultrasound attack. Therefore, more synergistic SCOD should be released at higher NaOH dosage. Using size exclusion chromatography and fluorescence excitation-emission matrix spectroscopy, Tian et al. [23] also indicated that synergistic solubilization of humic acids like substances took also place during the combined pre-treatments which can explain the increase in SCOD concentration. It was hypothesized that cavitation forces disrupted bioflocs in the sludge matrix and released the enmeshed humic acids. In turn, these substances which are not soluble otherwise, became soluble at alkaline pHs.

Even though no SCOD increase was observed after a single 0.01M NaOH addition (Figure 1), a considerable synergistic effect was achieved in the combined treatment. The synergistic effect became stable when NaOH concentration was beyond 0.02M. It is

therefore suggested that the presence of NaOH promoted the chemical effect of ultrasound (i.e. hydroxyl radical generation) and caused more COD solubilization. In other words, sodium hydroxide is believed to have a catalytic effect for hydroxyl radicals generation during ultrasonication meaning that hydroxyl ions will assist ultrasonication to produce more highly oxidative radicals. During the first two minutes of NaOH addition, the catalytic effect was obvious due to hydroxyl ions which led to significant synergistic COD release. However, with the chemical reaction between NaOH and sludge, the synergistic effect became insignificant due to lack of "catalyst". This is because radical's generation is a result of cavitation bubbles formation [34]. When the hydroxyl ions concentration is too low, there will be not enough ions in the vicinity of cavitation bubbles to promote radicals generation.

3.5. Process optimization

Based on this new theory, the conventional ultrasound/NaOH treatment was modified to a combination of stepwise NaOH addition and ultrasound treatment to optimize the synergistic effect. As the minimum NaOH dosage needed to reach the best synergistic effect was 0.02M, NaOH amount for each addition was 0.02M. The second batch of NaOH was added after five minutes of ultrasonication when the synergistic COD solubilization of first batch was known to cease. The optimized results are shown in Figure 4. The increase in SCOD is defined as the SCOD difference before and after disintegration (SCOD+). The physical meaning for SCOD+ is the substance that can be readily used to produce methane in the anaerobic digestion (Wang et al., 2005).

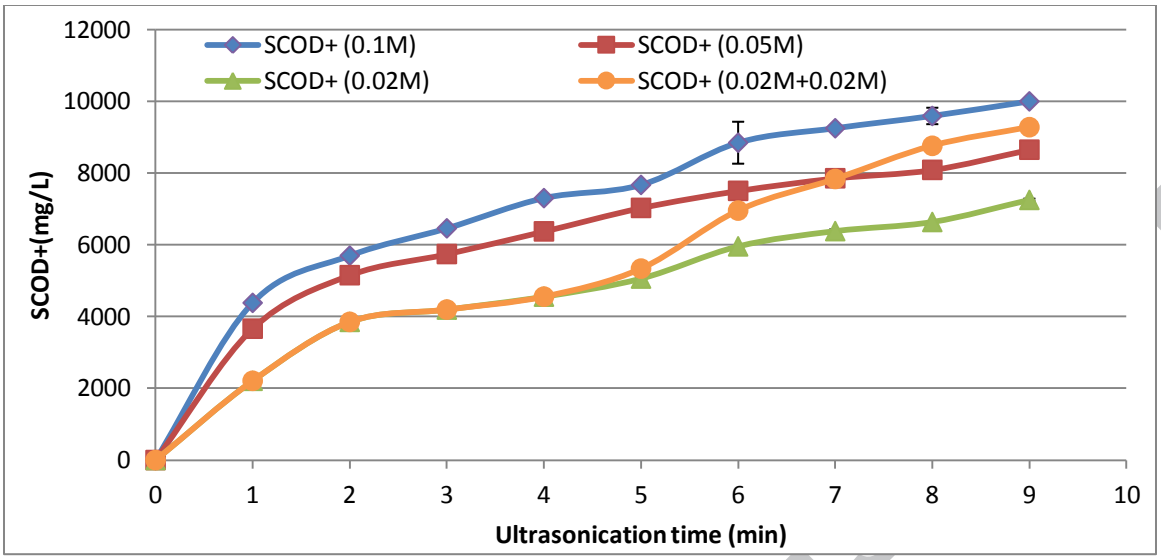


Figure 4. Comparison of conventional NaOH treatment and novel stepwise NaOH treatment (0.02M at time 0 and 0.02M after 5 minutes). The error bars represent the standard deviation associated with SCOD measurements.

It is clear from this graph that this novel two-step or stepwise addition of NaOH with continuous ultrasound treatment was more effective than conventional NaOH/ultrasound treatment. The solubilized COD for this novel treatment was higher than when 0.05M was added. The explanation behind this is believed to be that the catalytic effect induced by the re-addition of "catalyst". The corresponding DD were 85% for the 0.02M+0.02 strategy versus 79.4% for the 0.05M dosage indicating a higher efficiency at a lower dosage (20% less NaOH). The TSS and VSS reduction were 23.2% and 22.6%, respectively, which are similar to the conventional combined pre-treatment: 24.2% and 21.8%, respectively. .

The influence of power density to this treatment process was also investigated and the results are shown in Figure 5. High power density produces more cavitation bubbles in a

specific volume of sludge [35]. When no NaOH was added, the performance of different power densities did not show obvious difference for the same specific energy input. Similar results were observed for NaOH concentration of 0.02M. However, when the NaOH concentration was 0.05M, more COD was solubilized at higher power densities. More cavitation bubbles are created in a specific volume of sludge at high power density [35]. Sufficient "catalyst" together with more cavitation bubbles were available for the radicals generation which led to more COD solubilization.

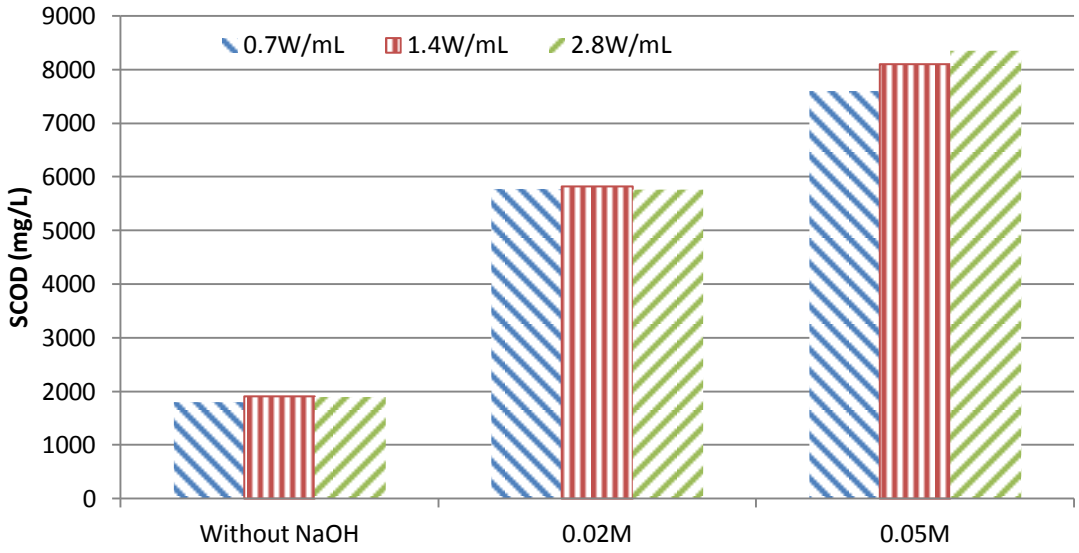
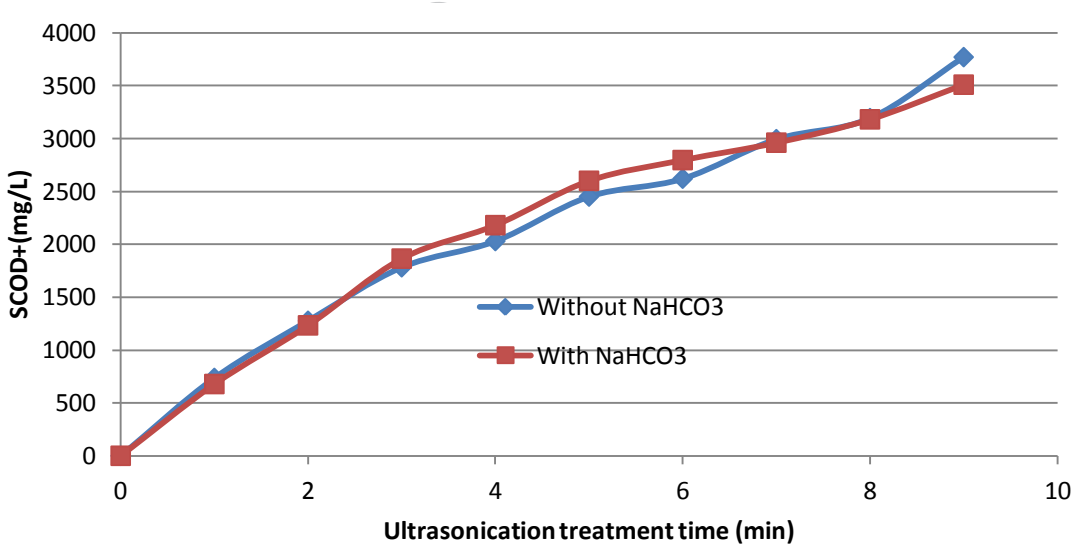


Figure 5. Influence of power density on combined NaOH/ultrasound treatment. (TS=17.2 g/L)

3.6. Effect of OH radicals scavenger

Since the combined NaOH-ultrasound pre-treatment is based on the optimized exploitation of OH radicals, it is relevant to investigate the addition of $NaHCO_3$ which is known to be a scavenger of OH radicals. Wang et al. (2005) added $NaHCO_3$ to the sludge

before ultrasound disintegration to mask the oxidizing effect of OH radicals, so thatthe disintegration can be thought to be the effect of hydro-mechanical shear forces only. They found that hydro-mechanical shear forces caused by ultrasound was predominantly responsible for the disintegration, and the contribution of oxidizing effect of OH radicals increases with the amount of the ultrasonic density and intensity. This was confirmed in Figure 6 (top) where the addition of $NaHCO_3$ did not affect significantly the increase of SCOD concentration which means that the original effect of radicals during ultrasonication alone is low. However, during the combined NaOH-ULS treatment (Figure 6 bottom), the synergic effect slowed down due to $NaHCO_3$. This indicates that the addition of $NaHCO_3$ inhibited the synergic effect mechanism which is due to OH radicals.



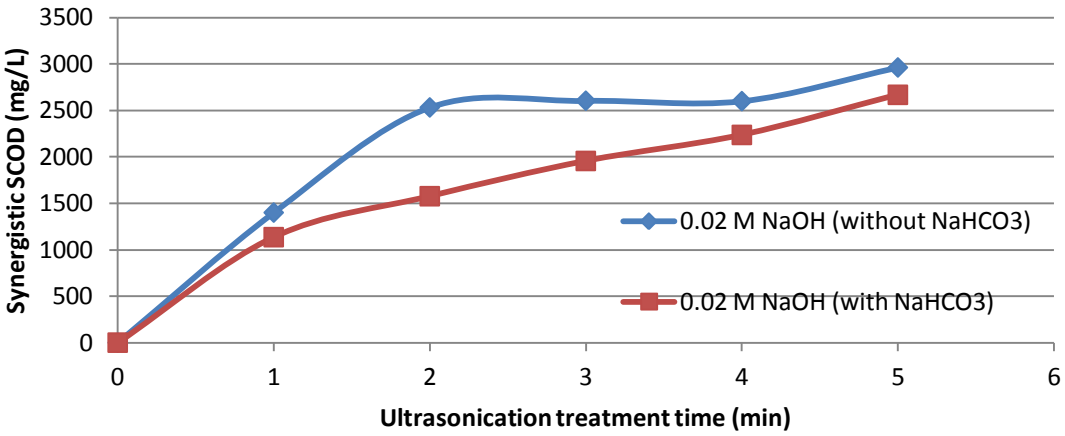


Figure 6. (top) Increase in solubilized SCOD during ultrasonication with and without OH radical scavenger $NaHCO_3$ (0.02M). (Bottom) Synergistic SCOD during the combined NaOH(0.02M)-ULS treatment with and without OH radical scavenger $NaHCO_3$ (0.02M). The error bars are smaller than the marker and were omitted on the graph.

3.7. Anaerobic biodegradability

The impact of the treatment on the SCOD and biodegradability of the sludge was compared in Table 4. 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/NaOH treatments were tested to investigate the synergistic effect on methane production. Both conventional (0.05M+ultrasound) and novel (0.02M+Ultrasound+0.02M+ultrasound) treatment schemes were approached.

Table 4. Sludge characteristics comparison after ultrasound treatment, NaOH treatment and combined ultrasound/NaOH treatment (TS=17.2g/L)

Sample	**SCOD (mg/L) After pre-treatment**	**Biodegradability of sludge after anaerobic digestion assay (mL CH_4/g COD_{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

The BMP curves for the aforementioned treatment conditions are shown in Figure 7. In all cases, the methane productions in the first four days were much higher than raw sludge. This is because more organics are available in soluble form after NaOH and ultrasound treatments. However, NaOH (0.05M) treated sludge and raw sludge reached similar ultimate biodegradabilities. This indicates that residual particulates after NaOH treatment was still hard to hydrolyze, possibly because flocs were shown to remain large in size (Table 2). Such gas production profile was not observed when NaOH treatment was combined with ultrasound. It is suggested that after ultrasonication particulate organics are dispersed into small fragments and became readily accessible for hydrolysis.

Nine minutes ultrasonication caused a significant SCOD increase (~4,700mg/L) due to mechanical shear force, 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 past results reporting that sludge biodegradability was

proportional to SCOD concentration after ultrasonication [36], the sludge anaerobic degradability only increased to 24% which was insignificant compared to 20% increase after nine minutes ultrasonication. This suggests that some of the solubilized substances were still recalcitrant to anaerobic digestion.

With the presence of NaOH, the performance of ultrasound was enhanced. This is because the chemical characteristics of recalcitrant substances were changed under chemical attack. The conventional combined ultrasound/NaOH showed a 31% increase in anaerobic biodegradability, whereas 40% was achieved after the novel stepwise combined ultrasound/NaOH treatment. This represents a 20% savings (0.04M versus 0.05M) in chemicals with a concurrent higher biodegradability (40% versus 31% more than untreated sludge). Less chemicals will translate into lower operating costs and lower concerns of sodium contamination of the final biosolids.

This is a significant improvement compared to previous studies where SCOD increased from 2,000 mg/L to 5,000 mg/L and no significant change were observed in methane production after NaOH treatment (0.266 g NaOH/g TS, 2 hours) followed by ultrasound (16.8 kJ/g TS) pre-treatment, presumably because NaOH released recalcitrant compounds or generates inhibitory compounds [21]. The sequence of treatment (NaOH then ultrasound) may explain the disappointing results and based on our results, it is recommend to apply NaOH and ultrasound simultaneously to fully exploit the potential of radicals.

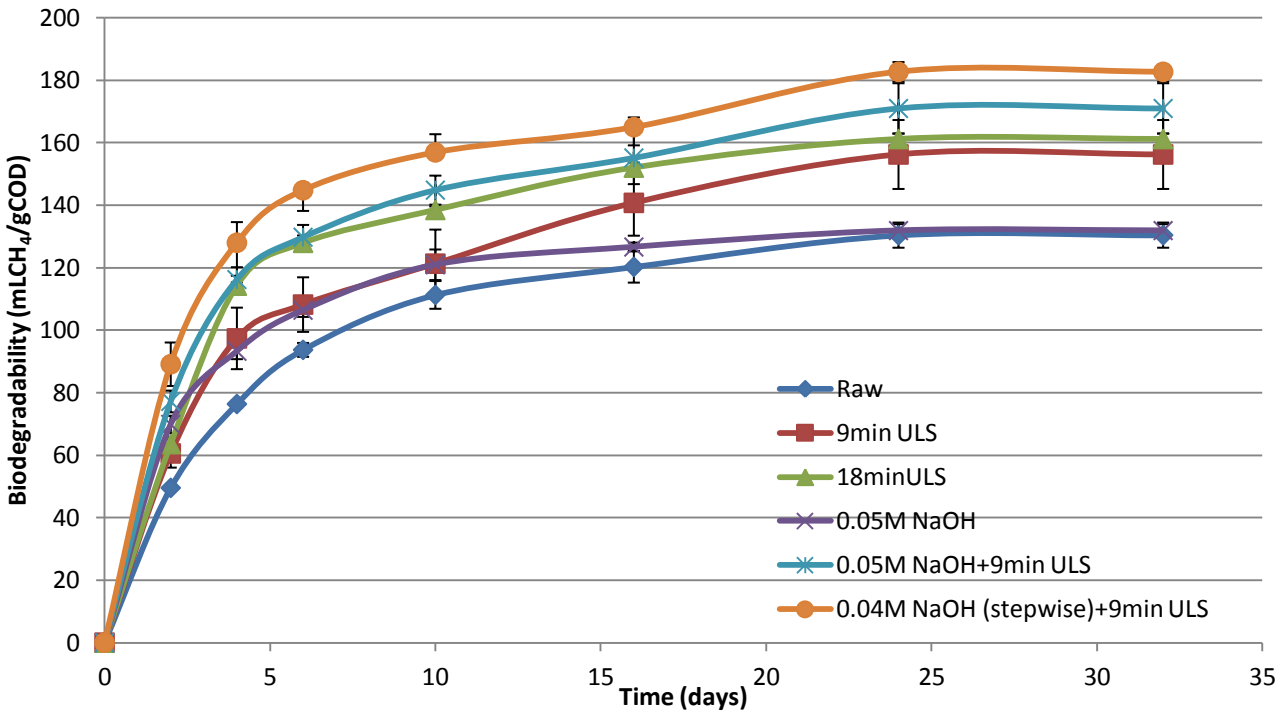


Figure 7. BMP curves for ultrasound, NaOH, combined ultrasound/NaOH and novel step wise NaOH addition/ultrasound pre-treatments. Error bars represent the standard deviation of triplicate BMP tests.

The combined ultrasound and stepwise NaOH addition treatment led to more methane production than conventional combined treatment. One possibility is that the second addition of NaOH caused more synergistic effect and led to more COD solubilization. More organics became available for fermentative bacteria and consequently for methanogens. Another possibility is that the stepwise NaOH addition accelerated the radicals' generation by ultrasound, and some recalcitrant compounds were hydrolyzed into smaller readily degradable compounds. Further investigation to determine the production of radicals and molecules change after this novel combined treatment is

recommended. A study on the effect of NaOH on premature pitting of ultrasonication probes or horns is also recommended.

4. Conclusions

Synergistic effect was observed when NaOH 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. 20% and 24% increase of methane production was observed after nine minutes and 18 minutes ultrasound pre-treatment respectively. Combined NaOH and ultrasound pre-treatment (0.05M+9min ULS) significantly increased anaerobic biodegradability of sludge by 31%. In the stepwise NaOH addition/ultrasound treatment, 20% less NaOH was consumed to achieve similar levels of COD solubilization and 40% increase in biodegradability was achieved.

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- combined ultrasound/alkaline pre-treatment of sewage sludge
- highest synergistic COD solubilization with 0.02M NaOH and five minutes ultrasonication
- (0.02M+ULS+0.02M+ULS) resulted in 40% increase of methane production.
- 20% lower NaOH consumption compared to one-shot addition
- Hydroxyl ions acts as catalysts for radicals generation by ULS