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Optimizing the synergistic effect of sodium hydroxide/ultrasound pre-treatment of sludge

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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 3000 mg/L was achieved on top of the NaOH (1975 mg/L) and ultrasonication (2900 mg/L) treatment alone. Further increase of NaOH dosage increased Soluble Chemical Oxygen Demand (SCOD), but did not increase the synergistic effect. Nine 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 (9 min + 0.05 M) 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.

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 30–40% 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 pretreat 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.

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Ruiz-Hernando et al. [8] compared NaOH, thermal and ultrasound pre-treatments and the optimum conditions were as follows: 27 kJ/g TS for ultrasound, 80 °C during 15 min 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. Park et al. [21] 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 (8–12) 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.

2.2. 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 µm 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]. 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.

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	700–1200
Soluble Protein	mg/L	< 100
Soluble Carbohydrate	mg/L	< 50

2.3. 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.

2.4. Ultrasonication pre-treatment

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

2.5. 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: 0.99 g/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 min 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 Fig. 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 1350, 1700, 3390 and 4830 mg/L after 9 min, 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% × (4830–900)/(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,