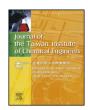
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### Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice



# Evaluation of thermal, thermal-alkaline, alkaline and electrochemical pretreatments on sludge to enhance anaerobic biogas production



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#### ARTICLE INFO

Article history: Received 25 March 2014 Received in revised form 27 May 2014 Accepted 29 May 2014 Available online 17 June 2014

Keywords: Anaerobic digestion Biogas production Pretreatment Sludge Stabilization

#### ABSTRACT

Anaerobic digestion was regarded as one of the ways to recover energy from waste activated sludge in this study. After applying thermal-, thermal-alkaline-, electrochemical- and alkaline-pretreatments to waste activated sludge to promote the digestion efficiency, biogas yield and volatile solid (VS) removal were investigated to evaluate the effectiveness of the pretreatments for the purpose. The highest biogas production (647 L/kg VS) was achieved after pretreatment by electrochemical method. The highest daily biogas production rate was obtained through alkaline pretreatment. Biogas production has no positive relationship with the solubilization degree of sludge. The highest VS removal rate could be got by the pretreatment of thermo-alkaline and electrochemical methods, and the sludge achieved the stabilization after the shortest digestion time with the treatment of electrochemical.

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#### 1. Introduction

The production of the waste activated sludge (WAS) is increasing as wastewater treatment increases and as environmental regulations pertaining to effluent quality become more stringent [1]. Sludge disposal and management can amount to 60% of the total cost of wastewater treatment; for this reason the minimization of sludge production is very important [2].

Various techniques for sludge minimization have been developed, including physical, chemical and biological technologies. Among these technologies, recently advanced anaerobic digestion with emerging pretreatment has created interest for enhanced biogas/methane production [3]. Anaerobic digestion (AD) is the biological breakdown of organic waste in the absence of oxygen, which advantages include: reduced sludge volume, sludge stabilization, sludge disinfection, and energy recovery in the form of methane [2].

Increasing sludge digestion through sludge disintegration can increase methane production, decrease sludge volume, reduce sludge retention time, and thereby improve the overall economics of the process [2]. Disintegration enhances the sludge hydrolysis rate by mechanically, chemically, thermally, or biologically aiding in the solubilization of sludge by rupturing cell walls/membranes [4].

In the last decade, different pretreatments have been proposed. WAS contains extracellular polymeric substances (EPS) and microbial cells that are resistant to AD due to slow and incomplete hydrolysis. So the hydrolysis of WAS is recognized as the ratelimiting step during the AD process [5], and as a result, many disintegration technologies have been applied in order to accelerate hydrolysis process or increase the degree of degradation including mechanical treatment [6], thermal treatment [7], freezethawing treatment [8], ultrasonic treatment [9,10], microwave treatment [11], chemical treatment such as Fenton, wet oxidation process, acid, alkaline, ozone, H<sub>2</sub>O<sub>2</sub> and biological treatment [8] all of which can work alone or combined together [12] prior to the AD of WAS to increase the soluble organic material available for AD.

As one of the newest sludge pretreatment technologies, electrochemical pretreatment has been previously tested for municipal WAS. Recent studies indicated that electrolysis at electrolysis time of 30 min, electric power of 5 W and initial sludge pH of 10 can effectively break down the EPS and increase the sludge reduction [13]. In addition to this, as a result of enhanced sludge disintegration and hydrolysis, electrochemical pretreatment increases the rate/extent of aerobic digestion, improves dewaterability [14–16]. However, there was no report about the electrochemical pretreatment prior to AD of WAS recently.

These pretreatments mentioned above can disrupt sludge flocs and cells, release inner organic matter, accelerate sludge hydrolysis and, consequently, improve the performance of subsequent AD. Since there are significant compositional differences among the sludges used in the different studies, a systematic comparison of

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pretreatment technologies is required to assess the viability during the AD process.

The objective of this study is to compare the impact of the four pretreatment technologies (thermal, thermal-alkaline, alkaline and electrochemical) on the extent of AD of WAS from a wastewater treatment plant (WWTP) in shanghai, China, in order to provide a new alternative of sludge pretreatment for sludge stabilization and energy recovery.

#### 2. Materials and methods

#### 2.1. Waste activated sludge sample

The WAS was obtained from secondary sedimentation tank of a municipal wastewater treatment plant (WWTP) in Shanghai, China. The plant treats  $20,000 \, \mathrm{m}^3$  wastewater per day using a anaerobic–anoxic–aerobic process. The collected sludge was sieved to remove matter coarser than 0.5 mm before use, and then centrifuged at  $2200 \times g$  for 3 min to obtain a total solid (TS) level of about 3%. The basic properties of the sludge were given in Table 1.

#### 2.2. Pretreatments of sludge sample

Several pretreatment methods such as thermal-, thermalalkaline-, alkaline- and electrochemical-treatment were selected from the preliminary study and literature review [17], and applied to enhance AD of WAS by partial destruction of cells.

Thermal-pretreatment was conducted for 9 h at 70 °C with a water bath (HBS-300, China). Thermal-alkaline pretreatment was conducted at a condition of 90 °C and pH 11 for 10 h. Alkaline pretreatment was adjusted to pH 10 by 5 N NaOH for 8 days. Electrochemical pretreatment was performed at the optimal conditions from our preliminary study. The electrochemical experiment of WAS was carried out in a 1L organic glass containers by using a highly stable power supply (WYJ. 5A 60V DC. Regulated Power Supply, Shanghai, China) with the air pump (AIR PUMP, X-6500) of 0.60 m<sup>3</sup>/h m<sup>3</sup> to mix sludge better. Both the anode and the cathode were pairs of Ti/RuO2 meshes plate electrodes of  $10.0 \times 13.0 \text{ cm}^2$  size. Sludge samples were treated with electrolysis voltage of 20 V, electrolysis time of 40 min, and the electrode distance of 2 cm. The dosage of sodium hypochlorite (NaClO) reagent with 0.6% (V/V) was also introduced to improve the electrochemical process. After pretreatment, all treated sludge samples were adjusted to pH 7.0 and stored at 4 °C before AD.

#### 2.3. Batch anaerobic digestion

Double-walled cylindrical vessels with 5 L working volume were filled with 2.5 L of pretreated WAS and 2.5 L of unpretreated sludge. Sample without pretreatment was set as the control. All digestions were repeated in triplicate. Before loading the sludge into the reactors, the initial pH of all the sludge was adjusted to about 7.0. The headspace was purged with nitrogen gas for 20 min to maintain anaerobic condition.

During the AD process, all the reactors maintained at a mesophilic digestion temperature of 35  $\pm\,2\,^\circ\text{C}$  by reciprocating

 Table 1

 Characteristics of WAS used in this experiment.

Parameter	Value
рН	$6.72 \pm 0.08$
Total solid (TS) (g/L)	29.3-32.4
Volatile solid (VS) (g/L)	19.1-22.5
Total chemical oxygen demand (TCOD) (mg/L)	29,245-32,165
Soluble chemical oxygen demand (SCOD) (mg/L)	96.2-435.3
Soluble total nitrogen (STN) (mg/L)	45.4-120.7
Soluble total phosphorus (STP) (mg/L)	15.2-38.9

water bath. Biogas volumes were measured by inserting an airtight syringe and allowing the plunger to equilibrate. A syringe was used to sample 0.2 mL of biogas to determine methane concentration by gas chromatograph.

#### 2.4. Analytical methods

Approximately 5 L of WAS was sampled for use in batch experiments. Sludge samples were characterized for TS and VS in duplicate by standard methods [18]. Sludge samples were centrifuged at  $22,000 \times g$  for 10 min and decanted to determine the soluble COD (SCOD). Supernatant pH was determined using a digital pH-meter (pHS-3C).

Soluble proteins were measured according to the Bradford method with bovine serum albumin (BSA) as standard [19], and soluble carbohydrates were determined by the Anthrone method with glucose as standard [20]. VFAs were analyzed by a gas chromatograph (GC-14B, Shimadzu) with a chromatographic column (DB-FFAP:  $30~\text{m}\times0.25~\text{mm}\times0.25~\text{mm}$ ) and a flame ionization detector (FID). Methane content was quantified with a chromatographic column (TDX-02) and a thermal conductivity detector (TCD).

#### 2.5. Statistical analysis

Standard statistical procedures were used, including standard deviation, mean averaging, and absolute difference between main and duplicate data points. When significant difference analysis was required, a single factor analysis of variance (ANOVA) or a one-sided t-test was used, with p < 0.05 considered significantly different.

#### 3. Results and discussion

#### 3.1. Effect of different pretreatments on the sludge properties

The properties of sludge have changed a lot when pretreated by different methods, such as pH, ORP, SCOD and TCOD (Table 2). The pH value of raw sludge decreased after thermal pretreatment. This is mainly due to the destruction of microbial cells by high temperature, leading to the release of intracellular substances. Hydrolysis and acidification of these organic molecules took place at high temperature with quicker rate, as a result, the pH value of the system dropped. In this experiment, the pH value of sludge pretreated by both thermo-alkaline and alkaline pretreatments keep a constant to 11 and 10, respectively. This is because

**Table 2** Variations of sludge characteristics after different pretreatments.

Pretreatment	Raw sludge	Thermal	Thermo-alkaline	Alkaline	Electrochemical
pН	$\textbf{6.72} \pm \textbf{0.08}$	$\textbf{5.21} \pm \textbf{0.03}$	$11.00 \pm 0.05$	$10.00\pm0.05$	$\textbf{7.94} \pm \textbf{0.10}$
ORP (mV)	$-112\pm4$	$-296\pm4$	$-403\pm8$	$-227\pm10$	$28\pm 6$
TCOD (mg/L)	$31{,}712 \pm 102$	$\textbf{28,822} \pm \textbf{69}$	$\textbf{28,255} \pm \textbf{76}$	$30,\!674 \pm 90$	$31,\!012 \pm 105$
SCOD (mg/L)	$124\pm 5$	$\textbf{8,924} \pm \textbf{43}$	$\textbf{13,929} \pm \textbf{68}$	$\textbf{16,053} \pm \textbf{65}$	$\textbf{7,284} \pm \textbf{47}$

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