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Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge

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ABSTRACT

The objective of this research was to develop an alkali pretreatment process prior to anaerobic digestion (AD) of pulp and paper sludge (PPS) to improve the methane productivity. Different concentrations of sodium hydroxide solution were used to pretreat PPS, and then followed by AD of PPS and monosodium glutamate waste liquor (MGWL).

Laboratory-scale experiments were carried out in completely mixed bioreactors, 1 L capacity with 700 mL worked. Optimal amount of sodium hydroxide for organics solubilization in the step of pretreatment was 8 g NaOH/100 g TS_{sludge}. Under this condition, the PPS flocs structure was well disrupted resulting in the void rate and fiber size decreased after pretreatment, and SCOD increased up to 83% as well as the peak value of VFA concentration attained 1040 mg acetic acid/L during AD. The AD efficiency of PPS with and without pretreatment was evaluated. The highest methane yield under optimal pretreatment condition was 0.32 m^3 CH_4/kg $VS_{removal}$, 183.5% of the control. The results indicated that alkali/NaOH pretreatment could be an effective method for improving methane yield with PPS.

1. Introduction

Anaerobic digestion (AD) of solid organic waste has gained increased attention as a means of producing energy-rich biogas, destructing pathogenic organisms and reducing problems associated with the disposal of organic waste [1]. AD is a multiple-stage process which is basically considered as three steps: hydrolysis, acidogenesis (fermentation) and methanogenesis [2]. In the hydrolysis step, insoluble organic material and higher molecular compounds such as lipids, polysaccharides, proteins, fats and nucleic acids are transformed into soluble organic materials. These smaller molecules are further broken down during the acidogenesis; the final products of this step are acetate, hydrogen and carbon dioxide. These molecules are the precursors of the methanogenesis; in this step, two groups of methanogenic organisms are involved into the methane production; one group splits acetate into methane and carbon dioxide, and the second group uses hydrogen as electron donor and carbon dioxide as electron acceptor to produce methane.

However, the application of AD to bio-solids were often limited by very long retention times (20–30 days) and a low overall degradation efficiency of the organic dry solids (30–50%). Those limiting factors are generally associated with the hydrolysis stage [3]. During hydrolysis, cell walls are ruptured and extracellular polymeric substance are degraded resulting in the release of readily available organic material for the acidogenic microorganisms. This mechanism is particularly important in the digestion of sludge, since the major constituent of its organic fraction are cells, being a relatively unfavorable substrate for microbial degradation [4,5]. The cell envelope of microorganisms is a semi-rigid structure which provides sufficient intrinsic strength to protect the cell from osmotic lysis. Microbial cell walls contain glycan strands cross-linked by peptide chains, causing resistance to biodegradation. Several authors, e.g. Refs. [6,7] have indeed identified hydrolysis as the rate-limiting step in AD of sludge.

Various sludge disintegration methods have hence been studied as a pretreatment to reduce the rate of the limiting step. These pretreatment methods that achieve a significant result in a lysis or disintegration of sludge cell have the potential to enhance the biogas production. Several methods have been studied in literatures with respect, including thermal [8–10], chemical [11–13], ultrasonic [14], mechanical [15] and biological [16–20]. While thermal pretreatment of sludge results in an increase in biodegradability, the thermal process consumes a substantial amount of energy in comparison to chemical consumption. Ultrasonic and enzyme pretreatment is also considered to be very expensive to get the high biodegradability rate. Previous studies have pointed out that alkali pretreatment is the best known method for enhancing the biodegradation of complex materials, such as lignocellulosic materials, thus rendering the most significant benefits [21]. Special attention is afforded to the use of alkali pretreatment for increasing

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Table 1
General characterization of the different waste used in the anaerobic test.

	TS (%)	VS (% of TS)	pH	OC (%, based on dry weight)	TN (%, based on dry weight)	C/N ratio
Pulp and paper sludge	31.45	62.3	7.82	32.75	1.09	30.05
Monosodium glutamate waste liquor	43.00	68.5	5.36	29.5	11.83	2.49
Inoculum sludge	9.17	53.2	7.85	26.70	0.71	37.61

the efficiency of anaerobic digestion of complex waste [22,23]. The preferred chemical, in the case, was sodium hydroxide (NaOH), which at relatively low dosage level is effective in solubilizing munitions-grade nitrocellulose into soluble organic carbon forms [24]. Lin et al. [13] demonstrated how alkali addition alone is capable of solubilizing waste activated sludge (WAS); tests were performed with sludge at 20 mg equivalent per liter (meq/L) NaOH (1% TS), 40 meq/L (1% TS) and 20 meq/L NaOH (2% TS) and the gas productions increased by 33%, 30% and 163%, respectively.

Pretreatments are to disintegrate the floc structure of sludge and extract both intracellular (within the microbial cell) and extracellular (within the polymeric network) materials before sludge is sent to the digesters. In most of the studies, pretreatments solubilized WAS, which subsequently improved anaerobic digestion of sludge. While AD is commonly practiced in the municipal sector, it has not mainly gained popularity in the pulp and paper industry. To the best of our knowledge, there is no full-scale anaerobic digestion facility in the pulp and paper sector for the digestion of solid residues [25].

In the late 1980s and early 1990s, several investigations were conducted to explore the use of anaerobic digestion treating pulp and paper solid residues [26–28]. The studies were performed on both laboratory and pilot-scale systems. The results of these studies generally showed that AD of pulp and paper bio-solids could reduce solid waste by 30–70%, with the benefit of methane production. Otherwise, due to the large amount of slowly digestible organics in PPS (e.g. lignin) and its long sludge residence times, high operating and requirement capital costs appeared to be the reason for the lack of subsequent mill installations. One fairly recent technological advancement that reduced the retention time requirement has been the development and establishment of pretreatment. Feasibilities of most of these pretreatment technologies have been demonstrated using municipal activated sludge (MAS). However, pulp and paper sludge (PPS) contains protein (22–52%), lignin (20–58%), carbohydrate (0–23%), lipid (2–10%), and cellulose (2–8%) [29]. Biological treatment of PPS has gradually become the main way instead of land filling and incineration [30]. In addition, compared with MAS, PPS contains higher volatile fraction which could make them more amenable to pretreatment technologies.

The objective of this study was to evaluate the biogas production capacity when pretreating PPS with alkali/NaOH prior to AD in a batch anaerobic digester, compared with untreated PPS (CK). Biogas productivity, organic removal and reactor stability were examined.

2. Methods

2.1. Materials collection and experimental procedure

PPS samples were collected from the primary and secondary clarifiers (normally settling tanks) of the Guangzhou Pulp & Paper Plant (China), which was usually dewatered to 60–70% moisture content at the end process of waste water treatment. Meanwhile, the seed sludge was obtained from the anaerobic digester of PPS started 3 months ago. In order to get the optimal C/N ratio, monosodium glutamate waste liquor (MGWL) was applied, which was collected from the Ao-Sang Monosodium Glutamate Factory (Guangzhou, China). For alkali pretreatment, 0.3%, 0.6% and 1.2% sodium hydroxide solution were prepared to soak PPS in the dosage of 4 g NaOH/100 g TS_{sludge}, 8 g NaOH/100 g TS_{sludge}, 16 g NaOH/100 g TS_{sludge}, according to the other study results [13,31,32]. PPS and MGWL were collected prior to each experiment, stored in the refrigerator (−4 °C) and analyzed for total solids (TS), volatile solids (VS), organic carbon (OC), total nitrogen (TN) and pH according to the standard methods for the examination of water and waste water [33]. Sodium hydroxide solution was made before the day when PPS pretreatment test carried out.

The first approach was the alkali pretreatment of PPS. In this step, PPS was divided into four portions with the same weight of 61 g. The first portion, the control sludge, was returned to the refrigerator for storage again. From the second to the forth portion, they were all soaked in 122 mL sodium hydroxide solution with the concentration of 0.3%, 0.6% and 1.2%, respectively. The solubilizations were carried out in 1000 mL Erlenmeyer flasks with working volume of 700 mL at 37 °C water bath for 6 h. Each reactor was kept in anoxia without the rubber stopper and stirring was done to ensure sufficiently dispersing the sodium hydroxide solution. After pretreatment, the control sludge was taken out from the refrigerator and all portions were ready to AD.

The second attempt was to carry out a batch AD experiment with PPS after pretreatment, MGWL and seed sludge. The chemical characterization of feedstocks was presented in Table 1. Changes in sodium hydroxide dosage and activity were shown in Table 2, which also displayed the dosage of other different waste to bioreactors (A–D). All bioreactors were filled with the same weight of feedstock at the amount of 700 g, in which distilled water was added in the end to keep the total amount up to 700 g. The chemical characterization of feedstocks was presented in Table 2. The feedstock for bioreactor A with no sodium hydroxide solution was a control (CK). AD of all four bioreactors began at the same time. The initial fermentation condition of AD experiment was C/N = 20, TS = 3%, inoculation amount = 10% of TS according to the feasibility study before [34]. The temperature was always maintained at 37 °C during this stage. Methane yield, alkalinity, total and volatile solids (TS and VS), soluble COD (SCOD), pH and volatile fatty acid (VFA) were measured during the period of AD experiment.

2.2. AD experimental set-up

8 lab-scale single-stage digesters were employed. Each bioreactor (used in pretreatment) had a gas-tight rubber stopper with an outlet equipped with methane collection and was flushed with N_2 for 5 min to replace the air (oxygen). The bioreactors were maintained at 37 °C in a water bath and shook by hand several times per day to assure the sufficient mixing to keep the feedstock from setting. The volume of methane from each bioreactor was measured by using a measuring cylinder, which was connected to the bioreactor. To remove CO_2, NH_3 and H_2O produced, an absorption flask with $Ca(OH)_2$ powder and a collecting gas bottle with 3% NaOH solution were collected between the two elements (Fig. 1). The methane produced displaced a measurable volume of water from the collecting gas bottle, which was equivalent to the methane volume [35]. All experiments were run in duplicate for 42 days.

2.3. Experimental analyses

The routine parameters were analyzed twice a week and all analyses were done by triplicate. TS, VS, pH, SCOD and alkalinity