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

Lin Yunqin*, Wang Dehan, Wu Shaoquan, Wang Chunmin

College of Natural Resources and Environment, South China Agricultural University, Guangdong, Guangzhou 510642, China

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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

* Corresponding author. Tel.: +86 020 85280302; fax: +86 020 85287672.
E-mail address: yqlin@scau.edu.cn (Y. Lin).

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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

Table 2
Composition of the feedstock used to pretreated PPS and then fed to four bioreactors digesting of PPS.

Bioreactor	Concentration of NaOH solution (%)	NaOH solution (mL)	Pulp and paper sludge (g)	MGWL[a] (g)	Inoculum sludge (g)	Distilled water[b] (mL)
A	0	0	61	2	23	122+492
B	0.3	122	61	2	23	122+492
C	0.6	122	61	2	23	122+492
D	1.2	122	61	2	23	122+492

[a] MGWL: monosodium glutamate waste liquor.
[b] Distilled water was divided into two part (connection with "+"); the first part was used to make 122 mL NaOH solution at three different kinds of concentration of 0.3%, 0.6% and 1.2%, respectively for PPS pretreatment and the latter part was added to each bioreactor to dilute total solids to 3% for PPS anaerobic digestion.

were determined according to the standard methods [33]; thereinto, SCOD were measured by potassium dichromate method. VFA were analyzed by distillation–titration method and the result was expressed in acetic acid [36]. The contents of cellulose, hemicellulose and lignin were measured by modified method of Wang and Xu [37]. Weighed 1 g sample into a 300 mL iodine flask, and then applied 100 mL neutral detergent. The iodine flask was placed into an autoclave sterilizer to heat insulated for 1 h, and then filtrated by 3# filter funnel buchner. The residue 1 was obtained after being washed by distilled water and acetone. The weight of residue 1 (W_1) was obtained after dried at 60 °C for 72 h. Place the residue 1 into a 300 mL iodine flask, and then added 100 mL 2 M HCl. The sample was placed into an autoclave sterilizer and heat insulated for 50 min at 100 °C. Residue 2 was obtained after filtrated by 3# filter funnel buchner, thereafter washed by distilled water to adjust the pH to 6.5–7.0. The weight of residue 2 (W_2) was got after dried at 72 °C for 72 h. Residue 2 was washed twice by acetone, thereafter dried at 60 °C, and placed into a 300 mL iodine flask. After added 10 mL 72% H_2SO_4, residue 2 was hydrolyzed for 3 h at 20 °C and then 90 mL by tap water was applied to keep in room temperature overnight. Residue 3 was obtained after filtrated by the weighted 3# filter funnel buchner and watered to adjust the pH to 6.5. The weight of residue 3 (W_3) was got after dried at 60 °C for 72 h. The W_4 was obtained after ashing the residue 3 at 550 °C. The calculation formula were as follows: hemicellulose (%) = $(W_1 - W_2)$/sample weight × 100%; cellulose (%) = $(W_2 - W_3)$/sample weight × 100%; lignin (%) = $(W_3 - W_4)$/sample weight × 100%.

3. Results and discussion

3.1. Pretreatment

3.1.1. The effect on chemical characterization of PPS

Table 3 showed the chemical characterization of PPS after bio-pretreatment. As organic matter in PPS was hydrolyzed during pretreatment; the increase of SCOD from 1664.0 mg/L to 20472.7 mg/L was noticed when the concentration of sodium hydroxide solution was increased to 1.2% (Table 2), and the greatest concentration of SCOD was 12 times more than CK. Under this condition, a destruction of sludge flocs was observed (Fig. 2). On the other hand, the concentration of volatile suspended solids (VSS) was decreased in the range from 6% to 19% after pretreatment, which may be due to the progressive hydrolysis of the complex organic matter present in the feeding. This result was consistent to the change of SCOD. Pumping filtration was needed to separate soluble substance away from the sludge before VSS was measured by drying samples in an oven until there was no any water in sludge (more SCOD, less VSS). Throughout the assay, the addition of sodium hydroxide caused an increase in NH_3-N on 45.9–62.4%, which can be produced by protein decomposition. Such behavior was also noticed by other authors [38]. Alkalinity in system results from the presence of the hydroxides, carbonates and bicarbonates of elements such as calcium, magnesium or ammonia [39]. The alkalinity helps to resist changes in pH caused by the addition of acids. In this pretreatment experiment, alkalinity of bioreactors with pretreated PPS were 2.5–19.6 times higher than CK. Pretreatment helped to lyse various kinds of inorganic matter such as carbonates ammonia and phosphates seemed to be a cause of the increased alkalinity, and the increase of NH_3-N also led to the increase of alkalinity. Higher alkalinity afford higher buffer capacity to avoid the decrease of pH [40].

The settling performance of sludge was expressed as sludge settling ratio (SV). The SV of bioreactors with sodium hydroxide were 56–192% higher than CK, which indicated that great swelling happed to PPS after pretreatment and the swelling intensified with the increase of sodium hydroxide solution concentration; the surface area of complex organic matter increased that made it more susceptible to enzymatic attack by microorganisms during AD. What is more, the supernatant after pretreatment was more turbid than that before pretreatment (the picture of gravity settlement was not shown in this paper), which indicated that more small molecular compounds produced after pretreatment, resulting in the colloids and dissolved solids in PPS increasing after pretreatment and remaining in supernatant which were not removed by settling.

3.1.2. The effect on flocs structure of PPS

Fig. 2 indicated that PPS flocs structure was disrupted, which became more compact with a little void ratio, and the crude fiber was obviously degraded into small units after pretreatment. Furthermore, the void ratio of sludge and the size of the fine fiber decreased with the increase of the alkali dosage. The result showed that alkali made sludge swelling and the structure loose; and then most of the macromolecule of PPS was degraded into monomers

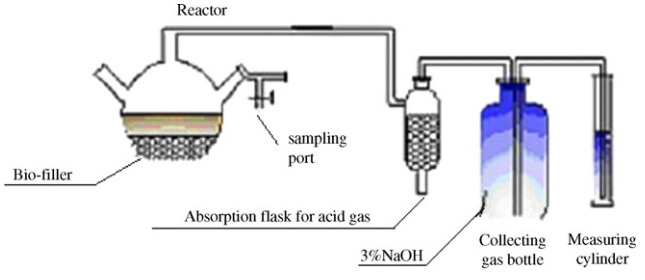

Fig. 1. The set-up of AD process.

Table 3
Chemical characterization of PPS after pretreatment.

Bioreactor	A[a]	B[b]	C[c]	D[d]
Alkalinity ($MgCaCO_3$/L)	504.19	2294.05	5256.15	10915.64
SCOD (mg/L)	1664.0	9028.8	14778.6	20472.7
VSS (of TSS)	39.93	37.60	35.76	32.15
NH_3-N (g/L)	0.85	1.24	1.38	1.24
SV_{ave} (%)	12.5	19.5	27.75	36.5

[a] AD of PPS without pretreatment (the control treatment).
[b] AD of PPS with 0.3% NaOH pretreatment.
[c] AD of PPS with 0.6% NaOH pretreatment.
[d] AD of PPS with 1.2% NaOH pretreatment.

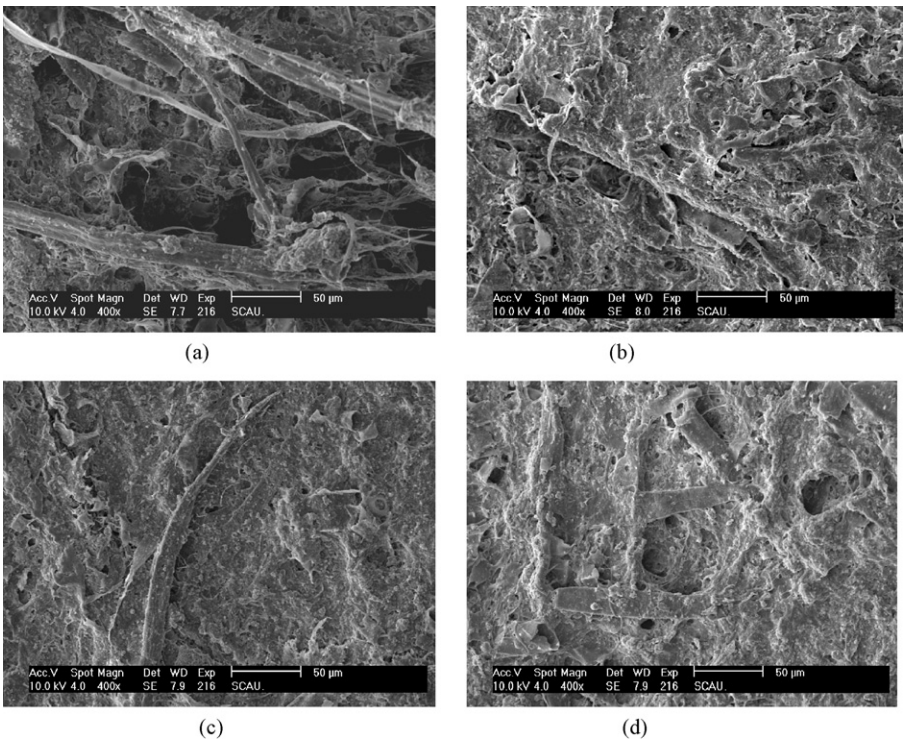

Fig. 2. Microphotograph of PPS before (a) and after (b–d) pretreatment at 30 bar (400×) (a–d: bioreactors A–D).

which would be easier to be decomposed by microorganism to increase the methane yield in the stage of AD. The same reports in the literatures were given by other authors [12,41].

3.2. Anaerobic digestion

3.2.1. Methane yield

The bioreactor fed with pretreated PPS had greater methane yield, and the methane yield increased as the concentration of sodium hydroxide solution increased (Fig. 3). The fractional increase of methane yield in bioreactors B, C and D was 54%, 83% and 88% over the control, respectively. The reason was that alkali pretreatment should increase not only organic solubilization, but also surface area available for enzymatic action as a result of improving anaerobic digestion performance. The concentration of sodium hydroxide solution in bioreactor D was the greatest, which caused a greatest methane yield. Similar results were summarized by other authors [12,13]. Comparing bioreactors C and D, the methane yield only changed a little (2.2%) between them; in contrary, the concentration of sodium hydroxide solution to pretreat PPS in bioreactor D was 2 times more than bioreactor C. The reason was that more Na^+ in bioreactor D could produce sodium toxicity to methanogens, which could be reduced by simultaneous addition of calcium and potassium in suitable concentration [32,42]. Taking economic (cost) and methane yield into consideration, the optimal sodium hydroxide dosage was 8 g NaOH/100 g TS_{sludge}. The cumulative methane production was shown in Fig. 3. The sequence of methane yield of each bioreactor on days 5–10 almost ranked in the order of $H_1 > CK > H_2 > H_3$ instead of $CK > H_1 > H_2 > H_3$ on days 0–4, but it changed to $H_3 > H_2 > H_1 > CK$ during the period of 11–42 days. The reason was that the bioreactor was unstable at the beginning of the anaerobic digestion which was the environmental adaptation stage for methane bacteria; more alkali added, more time was needed to adapt the new environment. The high concentration of sodium would inhibit the activity of the microorganisms and interfere with their metabolism [43,44]. When the system was stable, more methane yield was attained with bioreactor D because of more soluble organic material contained. Additionally, the methane production rate in each bioreactor with pretreated PPS reached the maximum on day 10 in the range from 97 to 219 mL/d, but the peak value was attained on day 19 at 80 mL/d in bioreactor

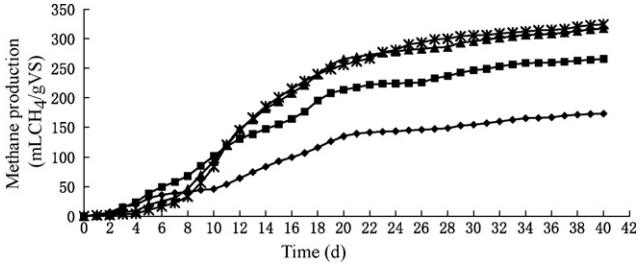

Fig. 3. Cumulative methane production (STP) for each bioreactor with PPS pretreated by different concentration of NaOH solution. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH (STP stands for standard conditions of temperature and pressure).

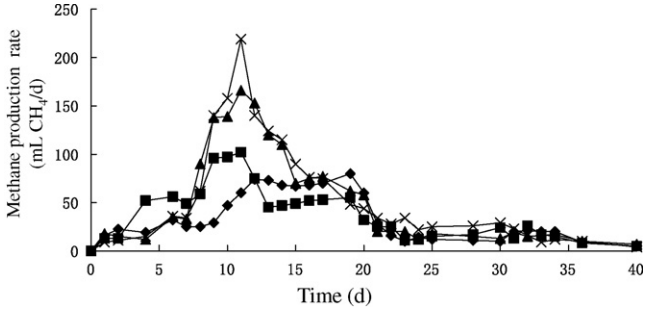

Fig. 4. Methane generation rate (STP) for each bioreactor with PPS pretreated by different concentration of NaOH solution. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH (STP stands for standard conditions of temperature and pressure).

Table 4
Comparison of the methane yield under different conditions.

	Tiehm et al. [3]	Chulhwan et al. [46]	Chulhwan et al. [46]	Lopez Torres et al. [12]	Sun et al. [47]	Lin et al. [34]	This study
Waste	WAS	WAS	WAS	OFMSW-not SS[a]	OFMSW-SS[a]	PPS	PPS
Pretreatment	Ultrasonic[b]	Biological[c]	Thermochemical[d]	Chemical[e]	–[f]	Biological[g]	Chemical[h]
CH_4 yield (m^3 CH_4/kg VS)	0.30	0.29	0.52	0.15	0.39	0.23	0.32

[a] SS: source selected.
[b] Waste activated sludge (WAS), ultrasonic disintegration.
[c] WAS, aerobic bacteria and acidogenic process with selected bacteria.
[d] WAS, thermal treatment with NaOH.
[e] Organic fraction of municipal solid waste (OFMSW), chemical hydrolysis with $Ca(OH)_2$.
[f] No pretreatment.
[g] Pulp and paper sludge (PPS), biological treatment with mushroom compost.
[h] PPS, chemical hydrolysis with NaOH.

A (Fig. 4), which indicated that alkali/NaOH pretreatment could increase methane yield and decrease the retention time of AD.

The peak value of methane yield was 0.32 m^3/kg $VS_{removal}$ at the standard temperature and pressure, which was higher than that from PPS, WAS and organic fraction of municipal solid waste (OFMSW) (not source selected) studied by other authors [12,34,45], but it was lower than that produced from source selected OFMSW which relied on a higher pretreatment cost and WAS with combination pretreatment which depended on the waste sorting collection (Table 4). The result showed alkali/NaOH pretreatment was effective to enhance methane yield for PPS anaerobic digestion. Generally speaking, organic carbon (OC) of PPS is mainly existed in cellulose, hemicellulose and lignin (Table 5), which are macromolecule and have complex structure; and they are difficult to be degraded directly by microorganism. Otherwise, alkali pretreatment could hydrolyze most of the organic material into solution to be used immediately in the anaerobic digestion process. Compared two different pretreatments to PPS (chemical and biological, see Table 4), the former enhanced more methane yield than the latter with a higher pretreatment cost, because the price of NaOH was much higher than EWMC which was extracted from the mushroom compost—a kind of solid waste from mushroom plants.

3.2.2. Organics removal

The bioreactors had varied rates of substrates removal in terms of SCOD, SCOD/TCOD, the content of cellulose, hemicellulose and lignin. Effective biodegradation in bioreactors was evidence in terms of SCOD removal efficiency, which attained the range of 83–93% in bioreactors with pretreated PPS compared with the control of 70% removal. Pretreatment offered advantage to obtain greater volumetric removal of organics. The peak values of actual SCOD concentration in each bioreactor were 2928.0 mg/L (bioreactor D), 2824.0 mg/L (bioreactor C), 2490.0 mg/L (bioreactor B) and 2290.0 mg/L (bioreactor A—CK), which reflected the hydrolysis of substrate was consistent to the alkali amount used to pretreat PPS.

As Fig. 5 showed, SCOD concentration of each bioreactor firstly increased and then decreased. The result was similar to other authors [48,49]. Compared with four bioreactors, the SCOD concentration increased in the bioreactor with the increasing sodium hydroxide dosage during the first period of AD (days 0–10); on days 11–32, the SCOD concentration decreased in the bioreactor with higher sodium hydroxide concentration used to pretreat PPS. The reason was that more sodium hydroxide produced more SCOD during pretreatment; so there were much more SCOD in the bioreactor D at the beginning of AD even though SCOD was further achieved by the acidogenic bacteria during this period; this phenomenon dominated and lasted about 10 days; on the other hand, there was much macromolecular compounds in PPS, such as cellulose, hemicellulose, lignin, etc. (Table 5) which could be hydrolyzed in a certain extent; so after 10 days, there was more hydrocarbons to be decomposed by extracellular enzyme in CK than other bioreactors, ranked in the order of $CK > H_1 > H_2 > H_3$; the SCOD content in the control bioreactor was also higher than others.

SCOD removal is a parameter that represents the degree of hydrolysis and solubilization achieved by the acidogenic bacteria. It was a little lower in this study than López Torres and Espinosa Llorens [12], mainly because there was more biodegradable organics in OFMSW than in PPS; but SCOD removal in this study was generally higher than those from others (Table 6), which indicated

Table 5
Percentage of cellulose, hemicellulose and lignin in PPS before and after anaerobic digestion (% of TS).

Bioreactor	Before AD	After AD			
		A	B	C	D
Cellulose	23.35	18.27	12.89	10.66	8.09
Hemicellulose	8.55	12.09	12.01	12.14	13.34
Lignin	16.51	15.98	15.90	15.55	15.58

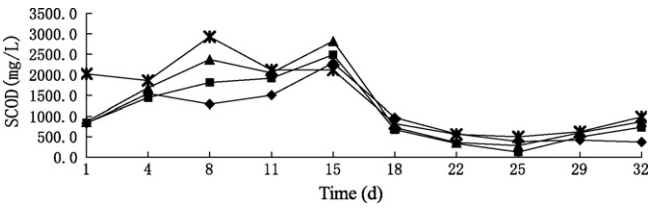

Fig. 5. SCOD changes in effluent for each bioreactor with PPS pretreated by different concentration of NaOH solution. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH.

Table 6
Composition of organics removal under different pretreatment methods.

Reference	Waste	Pretreatment	Comments during anaerobic digestion
López Torres and Espinosa Llorens [12]	OFMSW	Alkaline/$Ca(OH)_2$	Increase SCOD removal up to 93–94%
Lin [13]	WAS	Alkaline/NaOH	38–52% enhancement of SCOD degradation
Cristina [51]	Swine manure	Alkaline/NaOH	SCOD increased by 57%
Weemaes [50]	WAS	Ozonation	Increase of COD degradation up to 64%
This study	PPS	Alkaline/NaOH	Improved SCOD destruction ranged from 83% to 93%

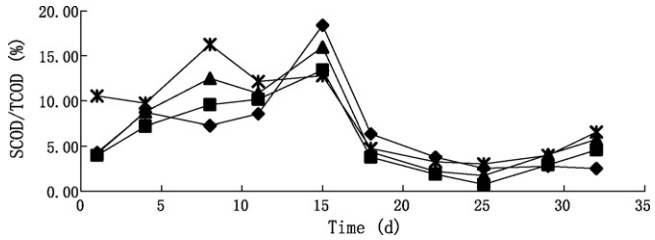

Fig. 6. The hydrolysis rate of PPS in each bioreactor. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH.

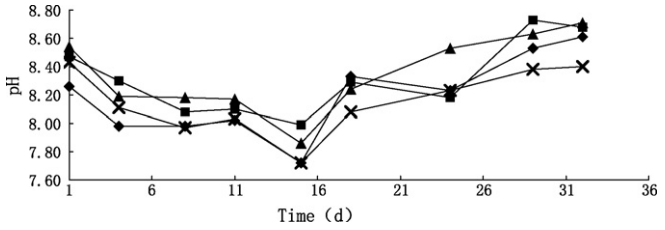

Fig. 8. pH value changes in effluent for each bioreactor with PPS pretreated by different concentration of NaOH solution. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH.

that alkali/NaOH pretreatment was more suitable to improve PPS hydrolysis before AD.

TCOD decreased by 21–24% during AD for four bioreactors (the data was not shown in the paper), resulting in continuous methane production (Fig. 3). The decrease rate was lower than SCOD (70–93%) mainly because there is some refractory organics in TCOD. SCOD/TCOD represented the hydrolysis rate of organics, whose change curve was similar to SCOD. On days 0–15, the SCOD concentration was higher in the average range from 830 mg/L to 2920 mg/L (Fig. 5), which was consistent with the greater hydrolysis rate on days 0–18 (Fig. 6), and the peak value of methane production per day was also attained on day 10.

Additionally, the cellulose contents of PPS in each bioreactor all decreased after AD (Table 5); the decrease rate was in detail of 21.76% (bioreactor A), 44.80% (bioreactor B), 54.35% (bioreactor C) and 65.35% (bioreactor D), which increased with the increased alkali amount; the result showed that applying alkali/NaOH to pretreat PPS would be favorable to degrade cellulose during AD. However, there was only a little difference of lignin contents in PPS after AD among each bioreactor and the lignin content of original PPS only varied a little after AD, which indicated that it was very hard to decompose lignin even though NaOH was added. Otherwise, the hemicellulose contents of PPS in each bioreactor all increased after AD and the same result was obtained in another literature [34], which should be studied further.

3.2.3. VFA concentration

Fig. 7 presented the VFA concentration of each bioreactor, which followed the same trend of SCOD curve (Fig. 5), as well as increasing firstly and then decreasing. The VFA concentration varied in a range of 365–1040 mg/L during anaerobic digestion. When VFA concentration started to decrease, methane generation rate increased [52]. The peck value of VFA concentration for each bioreactor was almost attained on day 8 (Fig. 7), which was uniform to the greatest methane generation rate occurred on day 10 (Fig. 4). For control run, as well as for bioreactors fed with pretreated PPS, the highest performance of VFA production in terms of concentrations were observed in bioreactor C, and the lowest VFA concentration was observed in bioreactor A (CK), as well as the average VFA concentration of each bioreactor during the period of AD was 599.5 mg/L (bioreactor A), 626.0 mg/L (bioreactor B), 681.3 mg/L (bioreactor C) and 648.0 mg/L (bioreactor D). The average VFA concentration in bioreactor D was 4.9% lower than bioreactor C, but the average SCOD concentration of bioreactor D was 13% higher than bioreactor C (Fig. 5). The reason may be that too high concentration of sodium inhibited the acetogenesis in bioreactor D.

3.2.4. pH values and alkalinity

The fermentative microorganisms can function in a wider range of pH between 4.0 and 8.5 [53]. pH values in this experiment remained in the range from 7.7 to 8.7 during AD (Fig. 8), which were all more than 7 because the pH of original material added to the bioreactor was alkaline except for MGWL which addition amount was only 2 g. The pH curves of four bioreactors were similar, with dropping on days 0–15 and then rising on days 16–32; it was related to the variation of VFA concentration, that is, VFA produced during AD to reduce pH. During the initial digestion phase, pH dropped with VFA concentration increasing and continued to do so until reaching the lowest value on day 15, corresponding to a pH slightly above 7.7; with VFA consumption, pH values increased steadily until to 8.7.

pH cannot be an effective measure of the stability of an anaerobic process when there is a high buffering capacity. Small changes in pH occur when there are large changes in process performance [54]. Under this condition, alkalinity is used to reflect the process performance directly. The alkalinity of a steady system is between 1000 mg and 5000 mg $CaCO_3$ L^{-1} [40]. In this experiment, the alkalinity of the bioreactors with pretreated PPS were all much more than CK at the beginning of AD mainly in that sodium hydroxide solution was added to those bioreactors during pretreatment (Fig. 9). On days 0–4, the alkalinity of bioreactors B, C and D decreased sharply by 38.4%, 38.8% and 43.6% respectively, until to 1000 mg $CaCO_3$/L or so, which indicated the process was unstable in this stage; on days 5–12, the alkalinity steadily increased to the peak value in details of 1583 mg $CaCO_3$ L (bioreactor B), 1795 mg $CaCO_3$/L (bioreactor C) and 1788 mg $CaCO_3$/L (bioreactor D); additionally, there was only a little difference of alkalinity among bioreactors B, C and D, even though the concentration of sodium hydroxide solution used to pretreatment changed a lot; on the other hand, the alkalinity of the control bioreactor always increased from 120 mg $CaCO_3$/L to 1324 mg $CaCO_3$/L on days 0–12. The alkalinity of all

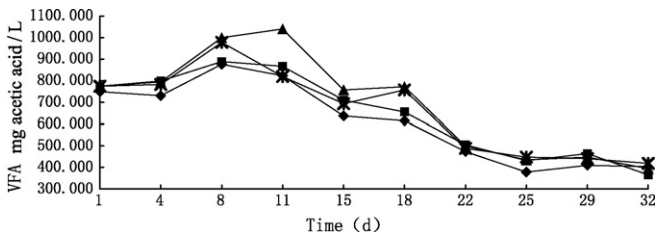

Fig. 7. VFA changes in effluent for each bioreactor with PPS pretreated by different concentration of NaOH solution. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH.

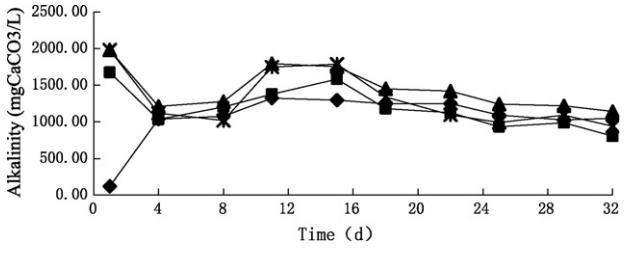

Fig. 9. Alkalinity changes in effluent for each bioreactor with PPS pretreated by different concentration of NaOH solution. (♦) CK, (■) 0.3% NaOH, (▲) 0.6% NaOH and (★) 1.2% NaOH.

bioreactors reduced very slowly after day 12, simultaneously keeping in a higher value (more than 1000 mg $CaCO_3$/L) until the end of AD to assure the steady of the process. In fact, the increase of alkalinity was normally due to the activity of the methanogenic bacteria, which could produce alkalinity in the form of carbon dioxide, ammonia and bicarbonate [55].

4. Conclusions

Four bioreactors were employed to evaluate the methane productivity when pretreating PPS with alkali/NaOH prior to AD at retention times of 42 days on 37 °C. Bioreactor A was fed with original PPS (as a control); bioreactors B, C and D was fed with PPS pretreated with different concentration of sodium hydroxide solution. PPS after bio-pretreatment had greater SCOD, VSS, SV_{ave}, NH_3-N and alkalinity. Methane productivity was enhanced by 54–88% when alkali/NaOH was employed as a pretreatment. The methane production of each bioreactor ranked in the order of $D \approx C > B > A$.

This study revealed that the best amount of sodium hydroxide used to pretreat PPS was 8 g NaOH/100 g TS_{sludge}, increasing methane productivity on 83% at a lower cost compared with other pretreatments. On the other hand, there may be sodium toxicity to the microorganisms which could interfere with their metabolism at the amount of 16 g NaOH/100 g TS_{sludge} to pretreat PPS.

Since the alkali pretreatment of PPS has shown promising results, more research will be carried out.

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