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Performance Enhancement Of Batch Anaerobic Digestion Of Napier Grass By Alkali Pre-Treatment

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Abstract: The objective of this research was to develop an alkali pretreatment process prior to anaerobic digestion (AD) of napier grass for improving solubilization of the lignocellulosic biomass and subsequent enhancement in biogas productivity. Mild concentrations of sodium hydroxide solution were used to pretreat napier grass which and was later subjected to anaerobic digestion for production of biogas. Laboratory-scale batch experiments were carried out in 0.5 l bottles with 0.3 l working volume. Optimal concentration of sodium hydroxide solution for organics solubilisation in the step of pre-treatment was 0.6% (w/v) i.e. 11.2g of NaOH/100g TS of napier grass. Under this condition, the soluble chemical oxygen demand of the hydrolysate was increased by 93%, which subsequently increased the production of volatile fatty acids (VFA) during anaerobic digestion. The biogas production of napier grass with and without pre-treatment was evaluated. The highest methane yield under optimal pre-treatment condition was found to be 0.158m^3 CH_4/kg TS, as compared to 0.047 m^3 CH_4/kg TS for untreated napier grass when subjected to anaerobic digestion for a period of 8 days. These results indicated that alkali pre-treatment could be an effective method for increasing biodegradability and improving methane yield of napier grass.
Keywords: Napier grass, Anaerobic digestion, Alkali pre-treatment, lignocellulosic biomass, biogas.

1. Introduction:

Anaerobic digestion (AD) has been very successfully employed by large number of countries over recent years for purposes such as energy production and waste management. Anaerobic digestion is a process where a consortia of microorganisms breakdown complex biomass in a series of reactions to produce biogas under anaerobic conditions. Various types of biomass such as

municipal biowaste, energy crops, industrial wastes and waste water and agricultural wastes have been explored over the years, as potential feedstocks for anaerobic digestion.

Harvest residues on an agricultural land may also be used as feedstocks in farm digesters provided the effluent can be applied conveniently to agricultural farm land. Such possible feedstocks for AD include plants and plant remains (e.g. leafs, corn, clover, stems etc.), spoiled or low quality fruits and vegetables, silo leachate and straw.

Napier grass (*Pennisetum purpureum*) is a species grown primarily for grazing. However, recently it has been incorporated into pest management strategy by growing it alongside the perimeter of the agricultural land to prevent stem borer moths from destroying the agricultural yield. Also, napier grass improves soil fertility and protects arid land from soil erosion. However, the remains of the napier grass represent a category of surplus lignocellulosic biomass.

Biomass or organic matter is converted into methane and carbon dioxide during anaerobic digestion by three bacterial groups in a series of complex biochemical process. Firstly, the hydrolysis and acidogenesis of the biomass is carried out by complex fermentative bacteria which hydrolyses polymers and ferments products to acetic acid and other organic acids, hydrogen and carbon dioxide. In the second step, the hydrogen-producing bacteria converts propionate and higher fatty acids, produced by the first group, into acetate and hydrogen in a process termed as acetogenesis[1]. Methane is generated, thus from acetate, hydrogen and carbon dioxide, by species of methanogenic bacteria during the final step termed as methanogenesis[2]. However, when treating particulate substrates such as solid waste, both the accessibility of hydrolytic microorganisms to the solid matter and hydrolysis of complex polymeric components constitute rate-limiting steps[3].

The primary biodegradable polymer in lignocellulosic biomass, cellulose, is shielded by lignin, a relatively inert, three-dimensional polymer of polyphenylpropane[4], and by hemicellulose[5]. The lignin, hemicellulose and cellulosic composition of napier grass is 111.8, 195.5 and 420.8 g/kg dry matter respectively[6]. This complex structure of the biomass obstructs and delays the rate of biological degradation thereby increasing the retention times, reactor volumes, and thus, capital costs in its large-scale application. The rate of biogas production can be improved by promoting the extent of hydrolysis of the organic matter by pre-treatment of the substrate.

Pre-treatment methods such as thermal hydrolysis[7,8] acid hydrolysis[9], alkali hydrolysis[10], ultrasound disintegration[11] and biological treatment[12,13] have been studied for breakdown of lignocellulosic biomass. The objective of this research is to enhance the biodegradability of the lignocelluloic biomass present in napier grass and subsequently improve biogas production.

2. Materials and Methods

2.1 Materials: Napier grass was obtained from cultivated on Kirloskar Oil Engines Limited, Pune campus. The plants cut were already dry, prior to harvesting. They were chaff-cut and stored dry. Stored Napier grass was pulverized into small particles (2 mm) before use. Anaerobic sludge for inoculum was obtained from an anaerobic digester acclimatised for lignocellulosic biomass utilised at Kirloskar Integrated Technologies Ltd. The characteristics of napier grass and inoculum is summarised in table 1.

2.2 Methods:

2.2.1 Alkali hydrolysis: For alkali pre-treatment, 0.3%, 0.6% and 0.9% sodium hydroxide solution were prepared to soak napier grass in the dosage of 5.6 g, 11.2 g and 16.8g NaOH/100 g TS Napier grass. Dried napier grass was soaked in the above alkaline solution with a solid loading of 5%. This reaction mixture was subjected to alkali hydrolysis at different temperatures 60°C, 70°C and 80°C by placing it on a hot plate for different periods of time ranging from 1-3 h.

2.2.2 Biogas potential tests: The reaction mixtures obtained after alkali hydrolysis with different conditions were subjected to batch anaerobic digestion. Batch AD was carried out in 0.5l glass infusion bottles with 0.3l working capacity. 200ml of anaerobic activated sludge was transferred into the glass infusion bottle. Hydrolysate and the solid residue obtained from alkali hydrolysis were added into the serum bottle. The infusion bottles were then sealed with butyl rubber tops and flushed with nitrogen for two minutes to remove as much oxygen as possible. The bottles were then incubated at 35 °C in complete darkness. Batch anaerobic digestion was carried out for a period of 8 days. All samples were analysed in quadruplets.

2.2.3 Analytical methods

Two of the quadruplet samples inoculated with similar substrate conditions were analysed for biogas

volume. The produced biogas was measured once every 24 hours. The bottles were shaken well by hand before measurement but any other form of mixing was absent. The gas volume was measured by water displacement method. The gas yields were calculated by measuring the gas production of the tested samples, then subtracting the gas production of the inoculum-only blind control.

The rest two serum bottles of the quadruplet samples were subjected to biogas composition testing by headspace analysis. Biogas composition was measured using a Thermo Scientific Trace GC 700 (Thermo Fisher Scientific India Pvt. Ltd, India) fitted with Hayesep Q 80/100 mesh column with a thermal conductivity detector. Hydrogen was used as carrier gas at a flow rate of 15ml/min. The column temperature was 40°C and then was raised to 140°C with a ramp of 15°C/min. The injector and detector temperature were 120 and 150°C. The compounds detected were methane, carbon dioxide, nitrogen and hydrogen sulphide.

The routine parameters were analysed everyday and all analysis were done by duplicate. Total solids (TS), Volatile solids (VS), pH, Soluble chemical oxygen demand (SCOD) and alkalinity were determined according to the standard methods[14]; thereinto, SCOD were measured by potassium dichromate method. Samples were withdrawn from the AD infusion bottles at regular interval of 24 hours to analyse VFA by distillation–titration method and the results were expressed in terms of equivalent acetic acid (mg/l)[15].

3. Results and discussions

The alkali hydrolysis was first performed at temperatures ranging from 70°C, 80°C and 90°C for 2 hours with different concentration of sodium hydroxide solutions. The SCOD, biogas and methane yield was quantified for each condition. It was found that the methane and biogas yield after AD was comparatively higher for pre treatment carried out at 80°C as compared to that carried out at 70°C (Table 1). Similarly, it was observed that there was not much difference observed when the pre-treatment was carried out at higher temperatures (Table 1). This shows that generation of SCOD, biogas and methane is more dependent on the concentration of alkali and the time of hydrolysis.

The same experiments were carried out for a prolonged period of treatment time i.e. upto 3 hours, with concentrations of sodium hydroxide ranging from 0.3% (w/v) upto 0.9%(w/v). It was observed that initially with 1 hour of treatment time, biogas and methane released after AD were significantly lower than those samples which were treated for 2 hours. However it was observed that there was no significant increase in biogas generation with the samples treated for 3 hours. From, table 2 it can be observed that the optimum alkali pre treatment parameters for maximum methane and biogas generation is 0.6% (w/v) of NaOH for 2 hours at 80°C.

Hereafter, alkali pre-treatment was carried out only at 80°C for 2 hours with different alkali concentrations to optimise the alkali concentration of the process. The AD bottle fed with untreated napier grass was termed Bottle A, the bottles fed with alkali pre treated napier grass with 0.3% NaOH , 0.6% NaOH and 0.9% NaOH were termed bottle B, C and D respectively.

Soluble Chemical Oxygen Demand (SCOD):

Table 1 and 2 depicts the soluble chemical oxygen demand obtained at various conditions of alkali pre treatment. The SCOD of the hydrolysate increased from 442 to 7140 mg/l when the concentration of sodium hydroxide was higher and time of hydrolysis was increased. The highest concentration of SCOD was 16 times greater than that obtained with untreated samples. It was visually observed that the volatile suspended solids decreased gradually, which may be due to the progressive hydrolysis of the complex biomass containing macromolecular compounds such as lignin, cellulose and hemicellulose[16].

Volatile fatty acid content:

The volatile fatty acid content (Acetic acid equivalent in mg/l) of each infusion bottle was measured at regular interval of 24 hours. The VFA concentration of the AD bottle fed with alkali pre treated napier grass at 80°C for two hours is presented in fig. 1. The VFA concentration varied in a range of 410–702 mg/L during anaerobic digestion. For untreated sample, as well as for AD bottles fed with pre-treated napier grass, the highest performance of VFA production in terms of concentrations were observed in AD bottle fed with 0.6% NaOH, and the lowest VFA concentration was observed in untreated napier grass, as well as the average VFA concentration of each bioreactor during the period of AD was 240.7mg/L (Bottle A), 316 mg/L (Bottle B), 363 mg/L (Bottle C), 323 mg/L (Bottle D). The average VFA concentration in bottle D was 12.5% lower than that of bottle C, but the average SCOD concentration was 20.5% higher than that of bottle C. The reason may be that too high concentration of sodium (NaOH) inhibited the acetogenesis in bottle D.

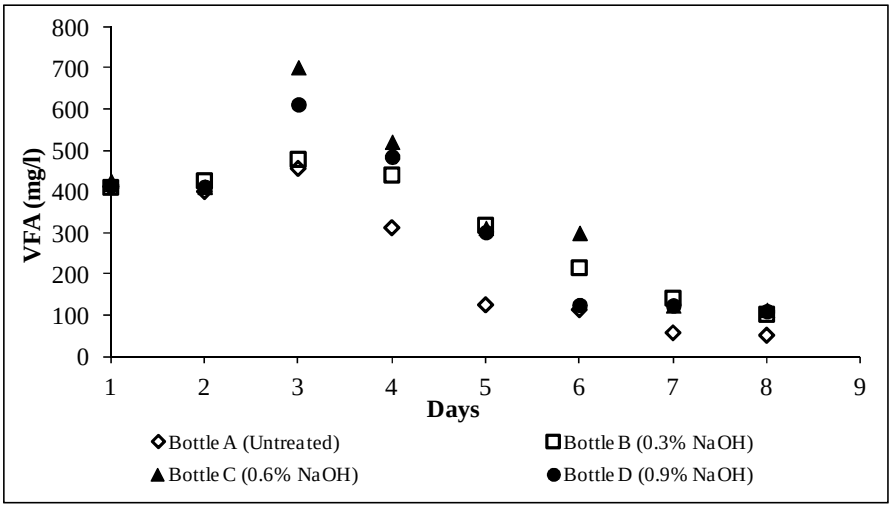

Figure 1: Volatile fatty acid concentration in mg/l for untreated and alkali treated napier grass. Alkali treatment at 80°C for two hours at different NaOH Concentrations.

Methane and Biogas yield:

Fig. 2 shows the cumulative biogas yield obtained from untreated and alkali treated napier grass samples. The data shown in fig. 2 is for the alkali pre-treated napier grass with different alkali concentrations at 80°C for two hours. The fractional increase of methane yield in bioreactors B, C and D was 43%, 70% and 68% over the untreated sample, respectively. The reason was that alkali pre-treatment should increase not only organic solubilisation, but also surface area available for enzymatic action as a result of improving anaerobic digestion performance. Similar results were summarized by other authors[16-18]. Comparing bottles C and D, the methane yield decreased, in contrary, the concentration of sodium hydroxide solution to pretreat napier grass in bottle D was greater than bottle C. The reason was the accumulation of sodium in bottle D could be toxic to methanogens and acetogens. Taking economic (cost) and methane yield into consideration, the optimal sodium hydroxide dosage was 11.2 g NaOH/100 g TS of napier grass i.e. 0.6% NaOH (w/v). The biogas production pattern is shown in Fig. 3. The biogas production was significantly low on the first day of the AD, 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[19-20]. When the system was stable, more methane yield was attained with bottle D because of the presence of more soluble organic material. Additionally, from fig. 4, it can be noted that the methane production rate in each bioreactor with pre-treated napier grass reached the maximum on day 3 which indicated that alkali/NaOH pre-treatment could increase methane yield and decrease the retention time of AD.

The peak value of methane yield was 0.158 m^3/kg TS (alkali pre-treatment with 0.6% NaOH (w/v)) at the standard temperature and pressure, which was higher than that untreated napier grass (0.046 m^3/kg TS). The result showed alkali/NaOH pre-treatment was effective to enhance methane yield for napier grass anaerobic digestion. Generally speaking, organic carbon (OC) of napier grass is mainly existed in cellulose, hemicellulose and lignin which are macromolecules and have complex structure; and they are difficult to degrade directly by microorganism. Alkali pre-treatment helped in hydrolysing and solubilising the organic material into solution to be used immediately in the anaerobic digestion process.

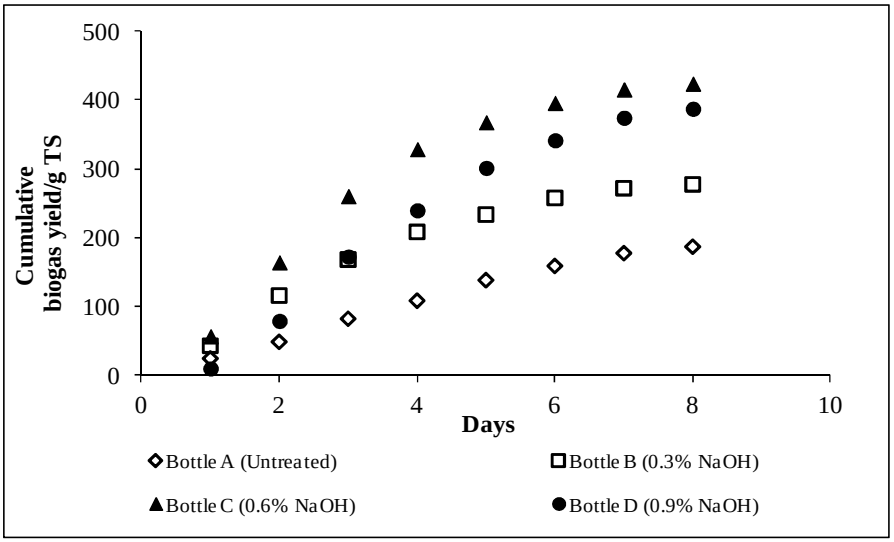

Figure 2: Cumulative biogas yield of untreated and alkali treated napier grass. Alkali treatment at 80°C for a period of two hours at different NaOH Concentrations.

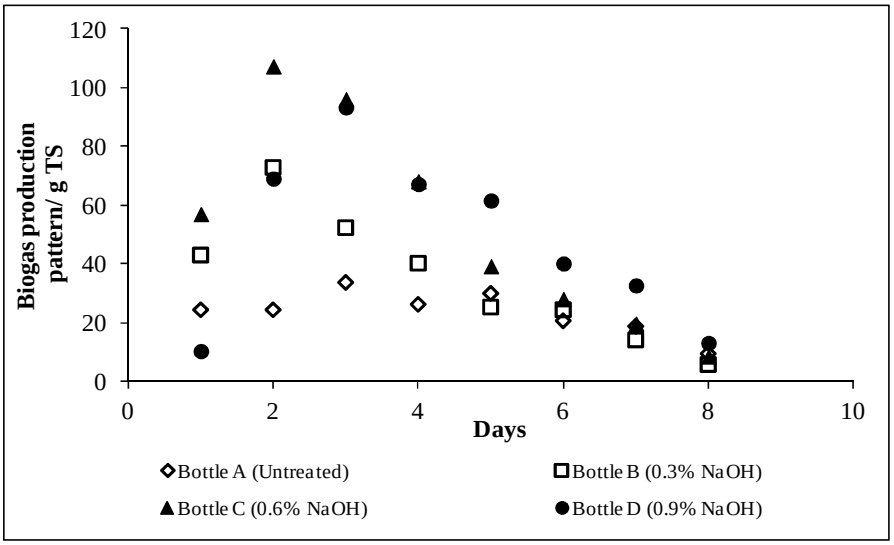

Figure 3: Biogas production pattern of untreated and alkali treated napier grass. Alkali treatment at 80°C for a period of two hours at different NaOH Concentrations

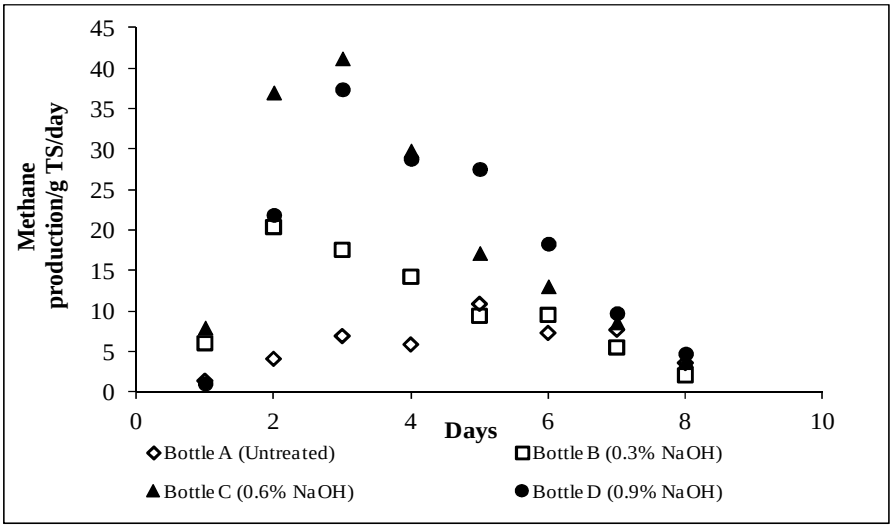

Figure 4: Methane production pattern of untreated and alkali treated napier grass. Alkali treatment at 80°C for a period of two hours at different NaOH Concentrations

Table 1: Characteristics of napier grass and anaerobic sludge inoculum

Parameters	Napier Grass	Anaerobic sludge inoculum
Total solids (TS)%	93.87	4.18
Volatile solids (VS)%	83.5	2.4
Total Organic Carbon %	43.8	24.7
Total Kjeldahl Nitrogen %	0.266	0.8
C:N ratio	190:1	30.8:1

Table 2: Soluble chemical oxygen demand, biogas and methane production from untreated and alkali treated napier grass. Alkali treatment was carried out for 2 hours with different NaOH concentrations and tempertaures

Parameters		SCOD (ppm) obtained after pre-treatment	Biogas (ml/g TS) production during AD	Methane (ml/g TS) production during AD
Untreated		442	171	46
0.3%	**70°C**	1232	239	80.5
	80°C	3812	236	84
	90°C	4124	240	90
0.6%	**70°C**	3123	318	133
	80°C	5417	382	155
	90°C	5614	390	157
0.9%	**70°C**	4217	339	155
	80°C	6820	346	146
	90°C	7140	352	151

Table 3: Soluble chemical oxygen demand, biogas and methane production from untreated and alkali treated napier grass. Alkali treatment was carried at 80°C with different NaOH concentrations upto 3 hours.

Parameters		SCOD (ppm)	Biogas (ml/g TS)	Methane (ml/g TS)
Untreated		442	171	46
0.3%	**1 hour**	1466	227	81
	2 hours	3812	236	80
	3 hours	4012	278	87
0.6%	**1 hour**	2011	342	122
	2 hours	5417	382	143
	3 hours	5674	391	154
0.9%	**1 hour**	3303	354	149
	2 hours	6820	346	155
	3 hours	7140	361	152

4. Conclusions

Alkali hydrolysis of napier grass was performed prior to batch anaerobic digestion at three different mild concentrations of alkali. The SCOD of the hydrolysate increased due to solubilisation of lignocellulosic biomass under alkaline conditions which subsequently increased the biodegradability and hence VFA and biogas production. Increase of alkaline concentration greater than 0.6% (w/v) decreased the yield of VFA and hence biogas production. It can be hypothesised that alkaline conditions with increased sodium concentrations may inhibit the propagation of acetogenic bacteria by rendering a toxic medium.

It was observed that under optimised conditions of 0.6% (w/v) NaOH treatment at 80°C for 2 hours, the SCOD of the hydrolysate was 5417mg/l. Further, when the hydrolysate along with the solid residue was subjected to batch anaerobic digestion for a retention period of 8 days, the methane productivity increased significantly. The methane productivity for untreated samples was 0.047m^3/kg TS and alkali treated sample under optimised condition was 0.158m^3/kg TS. These studies reveal that mild alkali hydrolysis can be an effective alternative for enhancement of biogas production for lingo cellulosic biomass.

5. References

1. Verstraete, W., de Beer, D., Pena, M., Lettinga, G., Lens, P., Anaerobic bioprocessing of organic wastes. World J Microb. Biotechnol., 1996, 12, 221–238.
2. Siegrist, H., Renggli, D., Gujer, W., Mathematical modelling of anaerobic mesophilic sewage-sludge treatment.Water Sci. Technol. 1993. 27 (2), 25–36.
3. Eastman, J.A., Ferguson, J.F., Solubility of particulate organic carbon during the acid phase of anaerobic digestion. J. Water Pollut. Control Fed. 1981 53, 352–366.
4. Sarkanen, K. V. and Ludwig, C. H. Lignins: Occurrence, Formation, Structure and Reactions, Wiley-Interscience, New York, NY.1971
5. Grohmann, K., Torget, R., and Himmel, M. E., Biotech. Bioeng. Symp. 1985.15, 59-80.
6. Ansah,T., Osafo E.L.K and Hanne H. Hansen. Herbage yield and chemical composition of four varieties of Napier (Pennisetum purpureum) grass harvested at three different days after Planting. Agriculture and biology Journal of North America. 2010, 1(5): 923-929
7. Jolis, D., Jones, B., Marneri, M., Kan, H., Jones,S., Panter, K., Thermal hydrolysis pre-treatment for high solids anaerobic digestion, in: IWA 10th World Congress, Montreal, Canada, 2004.
8. Skiadas, V.I., Gavala, H.N., Lu, J., Ahring, B.K., Thermal pre-treatment of primary and secondary sludge at 70 ◦C prior to anaerobic digestion, in: IVA 10thWorld Congress, Montreal, Canada, 2004.
9. Lise Appels, Ado Van Assche, Kris Willems, Jan Degrève, Jan Van Impe, Raf Dewil. Peracetic acid oxidation as an alternative pre-treatment for the anaerobic digestion of waste activated sludge. Bioresource Technology, 2011, 102 (5), 4124-4130
10. López Torres, M., Espinosa Llorens, M.D.C., Effect of alkaline pre-treatment on anaerobic digestion of solid wastes,Waste Manage, 2008, 28, 2229–2234.
11. Tiehm,A., Nickel,K., Zeuhorn, M., Neis, V., Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, Water Res. 2001, 35, 2003–2009.
12. Del Borghi, A., Converti, A., Pallazi, E., Del Borghi, M., Hydrolysis and thermophilic anaerobic digestion of sewage sludge and organic fraction of municipal solid waste. Bioprocess Eng. 1999, 20, 553–560.
13. Anthony Mshandete, Lovisa Bjo¨ rnsson, Amelia K. Kivaisi, S.T. Rubindamayugi, Bo Mattiasson, Enhancement of anaerobic batch digestion of sisal pulp waste by mesophilic aerobic pre-treatment. Water Research, 2005, 39,1569–1575.
14. APHA Standard Methods for the Examination of Water and Wastewater (19th ed.)American Public Health Association, Washington, DC, USA. 1995.
15. He Y.L. Anaerobic Digestion of Waste Water. Light Industry Press, Beijing, 1998
16. Lin Yunqin,Wang Dehan,Wu Shaoquan,Wang Chunmin. Alkali pre-treatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. Journal of Hazardous Materials.2009, 170, 366–373.
17. Wu, J., Xu, L.J., Xie, J.L.,The effect of alkali-pre-treatment on anaerobic digestion of solid organic waste (Chinese), Acta Scientiae Circumstantiae, 2006, 26 (2), 252–255.
18. Lin,J.G., Chang, C.N., Chang, S.C., Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilisation. Bioresour. Technol., 1997, 62 , 85–90.
19. Chen, Y., Cheng, J.J., Creamer, K.S., Inhibition of anaerobic digestion process: a review Bioresour. Technol., 2008, 99, 4044–4064.
20. Feijoo, G., Mendez, R., Lema, J.M., Sodium inhibition in the anaerobic digestion process: antagonism and adaptation phenomena. Enzyme Microb. Technol., 1995, 17, 180–188.

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