Desalination and Water Treatment
www.deswater.com
4 (2009) 224–228
1944-3994/1944-3986

Treatment of modified starch wastewater with high sodium chloride (NaCl) concentration using an anaerobic hybrid reactor

Kanlayanee Fusuwankaya[a], Pawinee Chaiprasert[a], Benjaphon Suraraksa[b]*

[a]*Department of Biotechnology, School of Bioresources and Technology, King Mongkut's University of Technology Thonburi (KMUTT), Bangkhuntein, Bangkok 10150, Thailand*
[b]*National Center for Genetic Engineering and Biotechnology (BIOTEC), Excellent Center for Waste Utilization and Management (EcoWaste), Bangkhuntein, Bangkok 10150, Thailand*
Tel. +662 470 7526; Fax: +662 452 3455; email: benjaphon@biotec.or.th

Received 10 December 2008; Accepted 10 March 2009

ABSTRACT

This work was designed to investigate the potential of an anaerobic hybrid reactor (AHR) in treating modified starch wastewater (MSW) containing high salt concentration. The AHR was started up by feeding native starch wastewater (NSW) until reaching a steady state at an organic loading rate of 4 kg COD/m^3/d and hydraulic retention time of 3 d. After that the MSW, to which was added a NaCl concentration of 2.5, 5.0 and 7.5 g/l, was fed into the AHR. The result was that the AHR yielded a high efficiency in treating the SMSW containing 5.0 g/l of NaCl. After increasing the NaCl to 7.5 g/l, the total volatile acid (TVA) was increased from 1,070 mg/l to 2,620 mg/l, whereas the alkalinity decreased from 1,950 mg/l to 705 mg/l. The TVA/alkalinity ratio was increased from 0.5 to 3.7, whereas the pH was reduced to 4.45. The amount of attached biomass and suspended biomass in the AHR was reduced from 71.1 and 90.7 g/reactor to 67.4 and 60.4 g/reactor, respectively. Moreover, the NaCl negatively affected the microbial activities inside the reactor, especially methanogenic activity. Contrarily, no inhibition was found when the 5.0 g/l of NaCl added. These results showed that the AHR was able to treat the modified starch wastewater containing 5.0 g/l of NaCl.

Keywords: Anaerobic hybrid reactor; Methanogens; Microbial activity; Modified starch wastewater; Sodium chloride

1. Introduction

Anaerobic digestion has become one of the most interesting treatment methods for highly organic polluted wastewaters. However, the application of this anaerobic technology can be applied in a wide range of wastewaters, such as wastewaters from vegetable canning, edible oil refining, the dairy industry, seafood processing, municipal solid waste landfill, and modified starch production, which may be hindered by the presence of sodium salts [1].

The tapioca starch industry is one of the major agro-industries in Thailand for internal consumption and export. There are 60 factories of native starch and modified starch in the country, and wastewater discharge varies from 13 to 50 m^3/ton of starch produced with an average of 20 m^3 [2]. Due to the demand of modified starch, the number of factories has been increased and expanded. The modified starch processes, especially in chemical modification such as hydrolysis, oxidation, cross

*Corresponding author.

Presented at the 1st Asia-Pacific Young Water Professionals (APYWP) Conference, 8–10 December 2008, Gwangju, Korea.

linking, and substitution, generate wastewater containing organic and inorganic matters that affect wastewater treatment efficiency. The modified starch production processes have rich amounts of sodium chloride (NaCl) in the wastewater due to the addition of chemical substances to the process (containing sodium) and the adjustment of the pH with hydrochloric acid (HCl). Consequently, the effluent from modified starch industries is at a high level of NaCl [3].

Wastewater with high concentrations of saline is often difficult to treat using the standard anaerobic treatment process. The presence of high sodium and/or chloride concentrations has been traditionally considered as inhibitory for anaerobic wastewater treatment [4,5]. Previous research has reported that high NaCl concentration causes plasmolysis and/or loss of cell activity, resulting to low efficiency in biological wastewater treatment and biogas production [6]. McCarty [7] reported sodium concentrations ranging from 3.5 to 5.5 g/l to be moderately and 8.0 g/l to be strongly inhibitory to methanogens at mesophilic temperatures. Kugelman and McCarty [8] and Gourdon et al. [9] reported that a sodium concentration exceeding 10 g/l strongly inhibits methanogenesis. Moreover, Ahring et al. [10] and Sowers and Gunsalus [11] noted that NaCl inhibits granulation and biofilm formation due to obstruct extracellular polysaccharide production. This result related to the study of Rinzema et al. [4]. They used upflow anaerobic sludge blanket (UASB) reactor in treating high salt wastewater and found that sodium concentrations of 5, 10, and 14 g/l caused 10, 50 and 100% inhibition of methanogens in anaerobic granular biomass, respectively, at neutral pH.

The anaerobic hybrid reactor (AHR) was developed to combine the advantages of UASB and anaerobic filter reactor for solving the limitations of these reactors in clogging, channeling and cell washout [12,13]. Moreover, the AHR has not been studied to any great extent for high salt wastewater treatment. Therefore, this study aims to apply the AHR in treating modified starch wastewater (MSW), which contains high NaCl concentration.

2. Materials and methods

2.1. Reactor design

The AH reactor was constructed from an acrylic pipe with an internal diameter of 9.4 cm and a height of 86.5 cm. The working volume and liquid level of the reactor were 5.55 l and 80 cm, respectively. The top half of the reactor height was filled with nylon fiber as a supporting medium and the rest of the reactor acted as a sludge zone (Fig. 1). The characteristics of the media are listed in Table 1.

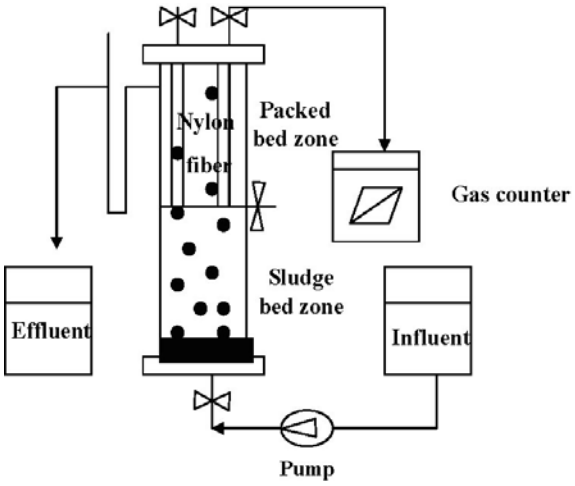

Fig. 1. Schematic representation of the AHR

Table 1
Characteristics of the supporting media

Type	Nylon fiber
Total weight (kg)	0.06
Surface area (m^2)	0.57
Volume (l)	0.06
Specific surface area (m^2/m^3)	10,130
Density at packed bed (kg/m^3)	26

Table 2
Characteristics of NSW and MSW

Parameters	Unit	NSW	MSW
Sodium chloride (NaCl)	(g/l)	0	2.5, 5.0, 7.5
pH		3.7–4.5	3.7–4.5
Alkalinity	(g/l)	0–0.25	0–0.25
Total volatile acids (TVA)	(g/l)	0.25-0.60	0.25–0.60
Suspended solids (SS)	(g/l)	5.7-7.9	5.7–7.9
Chemical oxygen demand (COD)	(g/l)	16–25	16–25
Phosphate	(g/l)	0.02–0.05	0.02–0.05
Ammonia	(g/l)	0.03–0.06	0.03–0.06
Sulfate	(g/l)	0.01–0.07	0.01–0.07

2.2. Seeding and wastewaters

A seeding concentration of 10 g/l obtained from a tapioca starch factory was inoculated into the AHR. The AHR was fed with starch wastewaters collected from a tapioca starch factory and then stored in a cold room at 4°C before being fed to the reactor. This storage technique had no observable effect on their composition. The starch wastewaters used were native starch wastewater (NSW) and MSW. The characteristics of these wastewaters are summarized in Table 2.

2.3. Operating conditions

To start up the AHR, NSW was continuously fed by gradually increasing the organic loading rate (OLR) at a hydraulic retention time (HRT) of 3 d. After the AHR reached a steady state at OLR of 4 kg COD/m^3/day and HRT of 3 d, the MSW, which was prepared by adding various concentrations of NaCl to the NSW, was fed into the AHR until failure. The reactor was operated under ambient temperature and fed in an upflow direction.

2.4. Analytical methods

The system's performance was followed according to standard methods [14] by measuring pH, alkalinity, total volatile acids (TVA), COD, and volatile suspended solids (VSS). Biogas production was determined using a water-replacement gas meter, whereas its composition was analyzed using gas chromatography equipped with a thermal conductivity detector (Shimadzu Chromatography, Model GC-9A).

The microbial activity of the biomass inside the AHR was measured by inoculating the biomass into different media depending on the microbial groups: 0.1% (w/v) of glucose for acidogens and 0.1% (v/v) of acetic acid for methanogens. After 5 days of 37°C incubation, the activity of each microbial group was interpreted considering glucose and acetic acid concentration. The utilization of glucose and acetic acid was determined with a lactate-glucose analyzer (YSI 2300 Stat Plus) and gas chromatography equipped with a flame ionization detector (Shimadzu Chromatography, Model GC-14A), respectively. Measurement of methane production was accomplished using water replacement and gas production with gas chromatography equipped with a TCD (model GC 14B, Shimadzu), respectively. The extent of the specific substrate utilization and gas production was indicated by the involvement of each trophic microbial group in the system.

3. Results and discussion

3.1. Performance of the AHR

The AHR was started up by feeding NSW (no NaCl) into the reactor. It reached an OLR of 4 kg COD/m^3/d and a HRT of 3 d within 4 months. The performances of the AHR showed high efficiency and stability. The pH, alkalinity, TVA, COD reduction, and methane yield were 6.85, 1622 mg/l, 850 mg/l, 90% and 0.35 m^3/kg$COD_{removal}$, respectively.

After reaching a steady state at OLR of 4 kg COD/m^3/d and HRT of 3 d, the MSW was fed into the AHR by increasing the NaCl concentration to 2.5, 5.0 and 7.5 g/l. The result is shown in Fig. 2. It was found that an increase of NaCl concentration in the MSW to 5.0 g/l did not affect the TVA accumulation or alkalinity in the AHR. After adding 7.5 g/l NaCl to the MSW, the TVA accumulation increased from 1,070 mg/l to 2,620 mg/l, whereas the alkalinity decreased from 1,950 mg/l to 705 mg/l. As a result, the ratio of TVA/alkalinity increased from 0.5 to 3.7, whereas the pH in the effluent reduced to 4.45.

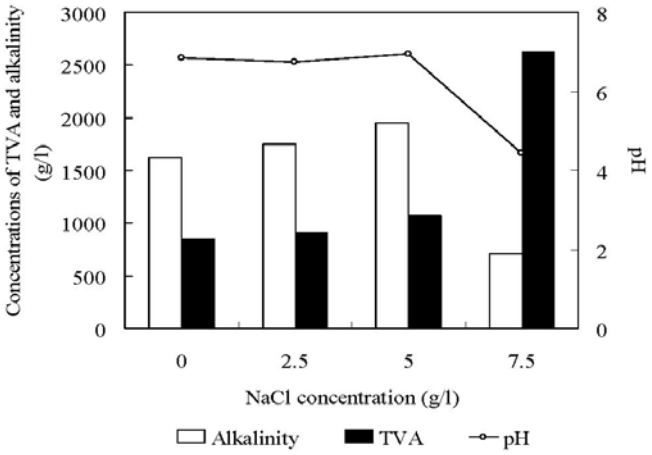

Fig. 2. Characteristics of the effluent in treating MSW adding various NaCl concentrations.

Table 3
Performance of the AHR in treating MSW containing various concentrations of NaCl at OLR of 4 kg COD/m^3/d and HRT of 3 d

NaCl conc. (g/l)	COD reduction (%)	Methane composition (%)	Methane yield (m^3/kg $COD_{removal}$)	NaCl conc. in effluent (g/l)
0	90	68	0.35	0.10
2.5	90	66	0.34	2.25
5.0	89	64	0.34	4.74
7.5	67	44	0.17	7.05

The performance of the AHR in treating the MSW containing various concentrations of NaCl is shown in Table 3. When feeding the MSW containing 2.5 and 5.0 g/l NaCl, the performance of the AHR was not significantly different from the treatment of NSW. After increasing the NaCl concentration to 7.5 g/l in the MSW, the AHR performance dramatically decreased, resulting in the reduction of methane composition and methane yield from 64% and 0.34 m^3/kg$COD_{removal}$ to 44% and 0.17 m^3/kg$COD_{removal}$, respectively. It can be seen that the poor reactor performance was affected by the salt. These results correspond with the previous study of Backus et al. [5], which reported the detriment of the anaerobic reactor caused by the presence of a high concentration of sodium ions. Moreover, there was a slight decrease of NaCl concentration in the effluent that can be explained by the

previous study of Kugelman and MacCarty [10], which reported that a sodium concentration in the range of 100–200 mg/l was beneficial for the stimulation of the acetate metabolism. Microorganisms can use the NaCl to be a trace element for their growth. As a result NaCl concentration in the effluent of the AHR was reduced.

The results displayed above show that the 5.0 g/l NaCl added to the MSW did not affect the performance of the AHR, whereas the previous study of Kugelman and MacCarty [10] reported that sodium concentration above 4600 mg/l (200 mM) was strongly inhibitory. Moreover, Rinzema et al. [4] reported that sodium concentrations of 5, 10, and 14 g/l caused 10, 50 and 100% inhibition of methanogenic activity of anaerobic granular biomass at neutral pH. It can be concluded from this result that the AHR yielded a higher efficiency than the UASB, in which granulation was affected by salt.

3.2. Biomass quantification in the AHR

An increase of NaCl concentration in MSW resulted in an increase of biomass washout, from 4.1 to 11.4 g (Table 4). Determining the amount of biomass in each concentration of NaCl found that the attached biomass and suspended biomass were reduced from 71.1 and 90.7 g/reactor to 67.4 and 60.4 g/reactor, respectively. These results show that the suspended biomass washed out from the AHR was higher than the attached biomass. It can be reasonably concluded then that supporting media play an important role in maintaining the biomass in a reactor. This result is related to the study of Chung and Choi [13], which reported the advantages of supporting media in the AHR.

3.3. Microbial activity in the AHR

Microbial activities of non-methanogens and methanogens in the AHR were investigated using a serum vial technique and the results are shown in Table 5. The microbial activities of non-methanogens and methanogens in treating NSW (no NaCl) were 1.148 and 0.350 gCOD/gVSS/d, respectively. When feeding the MSW containing 2.5 and 5.0 g/l NaCl, the specific microbial activity of each group was not significantly different from the treatment of NSW. After adding NaCl of 7.5 g/l to the MSW, the specific microbial activities of non-mehanogens and methanogens were reduced to 0.632 and 0.122 gCOD/gVSS/d, respectively. Moreover, the ratio of methanogens and non-methanogens was reduced to 0.192 when a NaCl concentration of 7.5 g/l was added.

These results showed that the activity of non-methanogens and methanogens decreased when NaCl concentrations were increased. This indicates that salt had an adverse effect on the microbial activities. The low activity of each microbial group detected could be the effect of salt on the inactivation of the cells from osmotic pressure. Most cells maintained an osmotic pressure in the cytoplasm that was higher than that of the surrounding environment, resulting in an outward-directed pressure, turgor, whose maintenance is essential for cell division and growth. Changes in environmental osmolarity can trigger the flux of water across the cytoplasmic membrane. Thus, in order to avoid cell lysis under low-osmolarity or dehydration under high-osmolarity growth conditions, cells must possess active mechanisms that permit timely and efficient adaptation to changes in the environmental osmolarity [15,16]. Even though non-methanogens and methanogens have evolved several strategies that enable them to survive and proliferate in environments of varied ionic composition and salinity, ranging from fresh water to hypersaline habitats [16,17], drastic changes in intracellular water density can result in the inactivation of microbial cells. Furthermore, increasing salt concentration reduces the concentration of water that is available to support biological growth. Since biological membranes are permeable to water, cells cannot maintain the water activity of their cytoplasm higher than that of the surrounding environment because this would lead to a rapid loss of water to the environment [18,19]. As a result, only organisms that have special adaptations can survive under extreme saline conditions. Moreover, in this study methanogens are sensitive to the salinity more than non-

Table 4
Biomass in the AHR at various concentrations of NaCl

NaCl conc. (g/l)	Biomass in the reactor (g/reactor)			Biomass washout (g)
	Attached biomass	Suspended biomass	Total biomass	
0	71.1	90.7	161.8	4.1
2.5	70.5	88.9	159.4	5.2
5.0	70.1	87.0	157.1	6.0
7.5	67.4	60.4	127.7	11.4

Table 5
Specific microbial activities of non-methanogens and methanogens in the AHR at various concentrations of NaCl

NaCl conc. (g/l)	Specific microbial activity (gCOD/gVSS/d)		Ratio of methanogens/non-methanogens
	Non-methanogens	Methanogens	
0	1.148	0.350	0.305
2.5	1.105	0.329	0.298
5.0	1.016	0.308	0.303
7.5	0.632	0.122	0.192

methanogens, resulting in a low ratio of methanogens and non-methanogens in the reactor.

4. Conclusions

At 7.5 g/l NaCl concentration, not only the performance but also the microbial activity in the AHR was dramatically decreased, especially methanogenic activity, resulting in the reduction of the ratio of methanogens/non-methanogens in the AHR. The imbalance of the microbial activity inside the reactor caused the failure of the reactor's performance, which resulted in low biogas production, low COD reduction, high TVA accumulation, low pH, and high biomass washout. However, the AHR can be used to treat the MSW containing NaCl of 5.0 g/l, which did not inhibit methanogenesis, whereas this concentration previously reported an inhibition of methanogenesis in the granule and biofilms of the UASB and AF, respectively.

From the results, it can be concluded that high NaCl concentration added to the AHR affected to the microbial activity, resulting to the performance of the reactor in treating MSW. Moreover, suspended biomass washed out from the AHR higher than attached biomass. This result indicated that the supporting media played an important role in maintaining the biomass in the reactor, and NaCl did not inhibit biofilms formation in the AHR.

Acknowledgement

This research was supported by a grant from Thailand Graduate Institute of Science and Technology (TGIST), program of National Science and Technology Development (NSTDA), Thailand.

References

[1] G. Feijoo, M. Soto, R. Mendez and J.M. Lema, Sodium inhibition in the anaerobic digestion process: antagonism and adaptation phenomena, Enzyme Microb. Technol., 17 (1995) 180–188.

[2] M. Tanticharoen, Research and development on agricultural biotechnology in Thailand [Online], Available: http://home.biotec.or.th/newscenter/Uploads/WE_pic/radC261F.pdf, 2004.

[3] O. Chavalparit and W. Limpaseni, Pollutant load from modified starch factories in Thailand, The Engineering Institute of Thailand Under HM The King's Patronage (EIT), Annual Conference, 1995, pp. 77–89 (in Thai).

[4] A. Rinzema, J. Van Lier and G. Lettinga, Sodium inhibition of acetoclastic methanogens in granular sludge from a UASB reactor, Enzyme Microb. Technol., 10 (1988) 101–109.

[5] B.D. Backus, C.J. Clanton, P.R. Goodrich and H.A. Morris, Carbon to nitrogen ratio and hydrauric retention time effect on the anaerobic digestion of cheese whey, Trans. ASAE, 31(1988) 1274.

[6] F. Kargi and A.R. Dincer, Enhancement of biological treatment performance of saline wastewater by halophilic bacteria, Bioprocess Eng., 15 (1996) 51–58.

[7] P.L. McCarty, Toxic materials and their control, anaerobic waste treatment Fundamentals—Parts III, Public Works, 1964, pp. 91–94.

[8] I.J. Kugelman and P.L. McCarty, Cation toxicity and stimulation in anaerobic waste treatment, J. Water Pollution Control Federation, 37 (1965) 97.

[9] R. Gourdon, C. Comel, P. Vermande and J. Veron, Kinetics of acetate, propionate and butyrate removal in the treatment of a semisynthetic landfill leachate on anaerobic filter, Biotechnol. Bioeng., 33 (1989) 1167–1181.

[10] B.K. Ahring, F. Alatriste-Mondragon, P. Westermann and R.A. Mah, Effects of cations on *Methanosarcina thermophila* TM-1 growing on moderate concentrations of acetate: Production of single cells, Appl. Microbial. Biotechnol., 35 (1991) 686–689.

[11] K.R. Sowers and R.P. Gunsalus, Adaptation for growth at various saline concentrations by the archebacterium *Methanosarcina thermophila*, J. Bacteriol., 170 (1988) 998–1002.

[12] J.A. Oleszldewicz and V.J. Thadani, Effects of biofilter media on the performance of Anaerobic Hybrid Reactors, Environ. Technol. Lett., 9 (1988) 89–100.

[13] Y.C. Chung and Y.S. Choi, Microbial activity and performance of an anaerobic reactor combining a fillter and a sludge bed, Water Sci. Technol., 27 (1993) 187–194.

[14] APHA, Standard Method for the Examination of Water and Wastewater, 19th ed., APHA/AWWA/WPCF, Washington, D.C., 1995.

[15] A.D. Brown, Aspects of bacterial response to the ionic environment, Bacteriol. Rev., 28 (1964) 296–329.

[16] D.M. Deana, A.C. Rose and F.R. Mary, Osmoadaptation in Archaea, Appl. Environ. Microbiol., 65 (1999) 1815–1825.

[17] G. Claude, A. Tjakko and R.B. Ian, Physiology of the osmotic stress response in microorganisms, Internat. J. Food Microbiol., 28 (1995) 233–244.

[18] A. Oren, Bioenergetic aspects of halophilism, Microbiol. Mol. Biol. Rev., 63 (1999) 334–348.

[19] R. Markus and M. Volker, Osmoadaptation in bacteria and Archaea: common principles and differences, Environ. Microbiol., 3 (2001) 743–754.