A Comparison of Anaerobic Treatment Performance of Fish Sludge in High-Saline and Low-Saline Environments Based on Volatile Fatty Acid and Biogas Production

Steven Dickey

Abstract

Mesophilic anaerobic treatment of undiluted ocean fish farm sludge (35% salinity) in continuously stirred tank reactors (CTSRs) was inhibited at sodium and chemical oxygen demand (COD) concentrations of 10.2 g/l and 60.3-74.1 g/l respectively. Only 36-55% of the COD could be stabilized before complete inhibition occurred. The high sodium content in the undiluted ocean water sludge, which prevented consistent physical contact between the bacteria and COD, did not inhibit hydrolysis or acidogenesis, but strongly inhibited acetogenesis, limiting the CTSR's ability to reduce the volatile fatty acids (VFAs) to acetic acid or carbon dioxide. The inhibition of acetogenesis led to low methane yields in terms of overall volume produced to amount of COD added (0.114-0.184 l CH_4/g of COD added), but the measured volume of methane in the sequestered biogas (45-65%) was as expected or only slightly lower than the previously observed value of 60%. These values suggested that acetogenesis is the rate limiting step and the only inhibited step in the anaerobic treatment of high saline fish sludge, limited by the physical limitations created by the high saline environment. When a 1:1 dilution of tap water to high saline sludge was attempted stable sludge conditions were established (282-466 mg acetic acid/l, 40-159 mg propionic acid/l) with a 60% minimum removal of COD added and a 60% methane concentration in the measured gas production. These observations from the Gebauer study compared to others suggested a maximum level of 17-35 g COD/l to establish a stable environment for anaerobic digestion of ocean water based sludge.

I. Introduction

Methanogenesis is a form of microbial metabolism in which a carbon source serves as a terminal electron acceptor and methane is formed. It is the final stage in the anaerobic digestion process and can only occur after acetogenesis reduces VFA to acetic acid or carbon dioxide (Ciborowski np). The methane gas resulting from the process is desirable for its energy generation potential. The reaction (applicable to this study) can occur by these two mechanisms:

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Several other compounds can exist as terminal electron acceptors preferential to the carbon dioxide and acetic acid due to chemistry (electronegativity, for example). Ammonia (NH_4) is an example of an inorganic molecule capable of serving as a terminal electron acceptor and sulfate (SO_4^{2-}) is an example of an organic molecule that can serve as a terminal electron acceptor. If the anaerobic digestion process is inhibited in any way the carbon dioxide and acetic acid available for methanogenesis will decrease, the VFA content of the sludge will increase to the point of instability, resulting in the inhibition and killing off of the methanogenic bacteria (Ciborowski np).

The research reviewed and discussed provided information about the inhibitory effects of a high sodium content sludge to the anaerobic digestion process. Success was evaluated based on the ability of the anaerobic digesters to sequester methane while meeting effluent requirements. Conditions evaluated included anaerobic digestion of high salinity, high COD concentration sludge from an offshore ocean water fish farm in Norway compared to a high salinity, low COD sludge from a separate offshore fish farm and a low salinity, high COD sludge from an onshore freshwater fish farm.

Ruth Gebauer performed research in 2003 to study stabilization of sludge from offshore salmon farms near Norway. The sludge accumulated as fish waste passed through membrane bioreactors utilized onsite as a primary wastewater treatment system. Onsite primary wastewater treatment systems at offshore fish farms became standard in the 1980s in Norway. The waste activated sludge accumulated from primary treatment at the fish farms was originally shipped by tanker to wastewater treatment plants for stabilization, but due to concerns of disease contamination from the transfer process and a desire to make the process more energy efficient the Norwegian Ministry of Agriculture recommended that the sludge be treated on site (Gebauer 155). Gebauer proposed that anaerobic treatment would be the preferable method due to energy saving potential and compared the methane production levels and sludge stabilization abilities of similar methanogenic species in the saline fish sludge to those of low saline fish sludge (Gebauer 163).

The methane production and VFA stabilization values observed by Gebauer in the high saline, high COD sludge were to be compared to values observed by Lanari and Franci from anaerobic treatment of a low saline, high COD sludge. The Gebauer study was unique because 70% of the solids in the saline fish sludge were suspended and a CRST reactor needed to be utilized to ensure high COD to bacteria contact. A CRST reactor was also selected over any type of bed reactor due to concerns of high settlement of sodium in the tank leading to a lack of COD to bacteria contact (Gebauer 156). The Lanari and Franci low salinity, high COD (40% suspended solids) study utilized an anaerobic up-flow digester (Lanari 289). Making a direct comparison of high saline to low saline anaerobic treatment was difficult because each type of sludge examined consisted of different load parameters, different reactor types and different values of potentially inhibitory constituents (sodium, sulphate and ammonia were concerns in this study). In order to make conclusions about the inhibitory effect of sodium on the anaerobic process, it was necessary to prove that the sulphate and ammonia concentration did not contribute to inhibition by examining observations made in other research projects.

The implications to large scale wastewater treatment in saline environments were discussed based on the influent characteristics and physical design of the anaerobic digesters examined. Several conclusions were made regarding the economic feasibility of treating fish sludge onsite at offshore fish farms.

II. Sulphate and Ammonia Concentration Concerns

The ammonia and sulphate levels in the undiluted Gebauer sludge were 2440-3040 mg total N/l and 920-1150 mg SO_4-S/l (Gebauer 157). The values were a concern because the initial inhibitory levels of ammonia (as noted by Gebauer) were established by several studies at 1500-1900 mg total N/l (McCarty, 1964; Melbinger and Donellon, 1971; Koster and Lettinga 1988). Also, Kugelman and Van Gorder (1991) observed strong ammonia inhibition in freshwater fish sludge at values of 2500-3500 mg total N/l. Because the objective of this paper was to compare the potential inhibition of high saline concentration on anaerobic digestion, it was necessary to show that the values of ammonia and sulphate concentration were not the inhibiting factor in the Gebauer anaerobic digester.

This concern can be addressed by noting that Soto et al. (1991), Mednez et al. (1995), Omil et al. (1996) and Punal and Lema (1999) reported stable anaerobic conditions utilizing high saline fish sludge of similar characteristics. The sodium, sulphate and ammonia concentrations ranged from 5-12 g/l, 0.6-2.7 g/l and 1-4 g/l respectively. The notable differences between the Gebauer study and the above mentioned (in this paragraph) were that the above mentioned contained only 20% suspended solids, while the Gebauer sludge contained 70% suspended solids (Gebauer 157). Also, the Gebauer study selected the CTSR reactor (to address the high suspended solids issue) while the above mentioned utilized an upflow bed reactor. The organic concentration of the Gebauer sludge was also 50-75% higher than that of the previous studies (Gebauer 156). The above mentioned studies are significant because they proved that anaerobic treatment and stabilization of high and low saline fish sludges was possible in the presence of potentially inhibitory levels of ammonia and sulphate.

III. Gebauer Results and Data

The bacteria utilized were methanosarcina barkeri and methanococcus varnietii (Gebauer 156). These mesophilic (35ºC) bacteria were developed from a municipal solid waste and cow manure inoculum fed to the reactors for 40 days at 1000 mg COD/l day (Gebauer 158). These methanogens were suitable and important for analysis because they are generally found in low-salinity digesters and thus provided an ideal comparison for the objective of this study.

Gebauer analyzed the methane production levels and stability of sludge of salmon farm sludge under anaerobic conditions. The parameters of concern were sodium (10200 mg Na/l) sulphate (920-1150 mg SO_4/l) and ammonia (2440-3040 mg N/l). The naturally occurring sulphate concentration from the ocean water and high ammonia concentration from the fish feces made the study more complex because the objective was to determine the inhibitory effect of the sodium concentration (issue addressed in section II).

The influent had the following characteristics:

Table 1. Characteristics of Gebauer Fish Sludge (Gebauer 157)

Component	Content
TS (wt%)	8.2–10.2[a]
VS (% of TS)	49.8–54.1[a]
Protein (% of VS)	29[b]
Fat (% of VS)	15[b]
Carbohydrates (% of VS)	56[b]
COD (g/l)	60.3–74.1[a]
Kj-N (mg/l)	2440–3040[a]
NH_4-N (mg/l)	430–530[a]
NO_3-N (mg/l)	2.2–2.7[b]
Tot-P (mg/l)	1350–1683[b]
Tot-S (mg/l)	990–1230[b]
SO_4-S (mg/l)	920–1150[b]
Na (mg/l)	10200[c]
K (mg/l)	476[c]
Ca (mg/l)[d]	4640 (1670)[c]
Mg (mg/l)	1759[c]
Cl (mg/l)	23600[c]

Table 2. Design Conditions (Gebauer 158)

Period	Days	Operating condition	SLV (ml)	OLR[a] (g COD/l day)	HRT[a] (days)
1a	1–57	First start up increase of sludge volume	3750–6100	1.0 until day 40, 1.55 from day 41	50.9
1b	58–95	Semi-continuous operation, withdrawal of sludge for serum bottle experiments on day 78 and following increase of sludge volume	3650–6000	1.38	61.5
1c	96–124	Semi-continuous operation, withdrawal of sludge for serum bottle experiments on day 118 and following increase of sludge volume	5150–6000	1.56	41.2
	125–191	*Stop of operation*			
2a	192–207	Increase of sludge volume	3500–4200	2.12	32.7
2b	208–232	Semi-continuous operation	4200–4000	2.55	27.5
	233–252	*Stop of operation*			
3	253–260	Semi-continuous operation	4000	1.9	65
	261–266	*Stop of operation*			
4a	267–282	Second start up with sludge from the reactor, increase of sludge volume	4000–6100	2.42	26.2
4b	283–337	Semi-continuous operation	5840–5240	2.52	27.9
5	*338–359*	*Stop of feeding*	5100–4600	0	∞
6a	360–363	Some feeding	4700–4900	1.44	48.1
6b	364–383	Semi-continuous operation	4900–4800	2.85	24.3
6c	384–402	Semi-continuous operation	4800	3.12	24.0
	402–404	*Stop of operation*			
7a	405–423	Third start up with sludge from the reactor, increase of sludge volume	4900–6000	1.15	54.4
7b	424–440	Semi-continuous operation	6000	1.24	60

The experiment was performed for several periods ranging from 7-124 days with low COD loading rates (Gebauer 163). The undiluted reactor was studied at hydraulic retention times (HRT) ranging from 24 to 65 days. The second diluted reactor was operated at a HRT of 30 days. Two digesters were loaded with the influent described in Table 1 (one digester was loaded with a 1:1 tap water to influent dilution). The salt ions listed accounted for the 35% saline composition in the first reactor and 17.5% salinity in the second, diluted influent reactor.

Table 3. Results Under Various Test Conditions (Gebauer 162)

Operating period	Undiluted sludge 6c	2b	4b	1c	7b	Diluted sludge 2b
Parameter						
HRT (days)	24.0	27.5	27.9	41.2	60	30
OLR (g COD/l day^{-1})	3.12	2.55	2.51	1.56	1.24	1.10
Length of period (days)	19	25	55	29	17	34
Feed						
COD_{in} (g/l)	74.9	70.1	70.0	64.2	74.2	33.7
TS_{in} (wt%)	9.36	9.43	9.19	9.4	10.18	4.51
VS_{in} (wt%)	4.90	4.92	4.81	4.76	5.51	2.30
% VS of TS_{in}	52.3	52.2	52.3	50.6	54.1	51.0
Sludge in digester						
COD_{out} (g/l)	39.5	29.7	40.6	29.2	37.5	13.6
TS_{out} (wt%)	6.51	5.79	6.67	5.09	6.21	2.88
VS_{out} (wt%)	2.40	1.97[a]	2.51	1.75	2.18	0.93
% VS of TS_{out}	36.9	34.0	37.6	34.4	35.1	32.3
Stabilization						
% COD removed	43.3	55.2	36.7	53.6	53.7	60
% VS removed	48.2	48.2	47.4	59.0	61.9	58
Gas composition						
vol.% methane	50.9	51.7	48.9	50.0	54.1	57.6
vol.% H_2S	2.3–3.5	2.5–2.8	2.8–3.6	2.4–3.3	2.2–2.5	1–1.6
Meth. Product. (STP)						
l methane/g COD added	0.136	0.161	0.114	0.165	0.184	0.154[b]
l methane/g VS added	0.201	0.221	0.160	0.215	0.241	0.220[b]
l methane/g COD removed	0.314	0.291	0.309	0.306	0.343	0.257[b]
l methane/l sludge added	10.1	11.3	8.0	10.6	13.7	5.2 (*diluted*)[b]
Vol. Meth. Prod. Rate (STP)						
l methane/l day^{-1}	0.414	0.409	0.286	0.256	0.228	0.174[b]
Spec. Meth. Prod. Rate (STP)						
l methane/g VS in dig. day^{-1}	0.017	0.020	0.011	0.014	0.010	0.019[b]

Methane production levels in the undiluted reactor were 0.114-0.184 l CH_4/g COD added and the propionic acid (VFA) content was measured as high as 5430 mg/l (Gebauer 162). The COD removal ranged from 32.6% at a HRT of 27.9 days to 52.6% at a HRT of 60 days (Gebauer 161). The conditions in the undiluted reactor were never stabilized over the entire 440 day duration of the research project.

The second Gebauer reactor, consisting of a 1:1 tap water to sludge dilution, reported successful, stabilized results. The diluted sludge consisted of 5600 mg Na/l, 460-525 mg SO_4/l and 1220-1520 mg N/l. The acetic acid content was stabilized at 282-466 mg/l and the propionic acid content was stabilized at 40-159 mg/l in the CTSR. 60% of the COD was removed in the diluted reactor. Gebauer believed the reported values for methane were in error, so no conclusion could be drawn about methane production in the diluted reactor (Gebauer 164).

The Gebauer observed values were to be compared to those values established by Lanari and Franci in 1998 for anaerobic treatment of fresh water fish sludge. Lanari and Franci observed highly productive rates of .4 l CH_4/g COD added at a similar COD loading rate and high COD concentration (Lanari 289). Lanari and Franci also observed stable conditions with an average of 1100 mg/l of VFA content in their upflow reactor (Lanari 291). Lanari and Franci were able to obtain COD removal of approximately 80% (Lanari 289). It was also observed that methane accounted for 80% of total gas production in the upflow reactor (Lanari 289).

III. Discussion

The low methane production levels in the Gebauer undiluted reactor (0.114-0.184 l CH_4/g COD added) and the high propionic acid content (5430 mg/l) can be attributed to inhibition due to the high sodium concentration of the ocean water sludge (Gebauer 162). The values suggested that the first two steps of anaerobic digestion (hydrolysis and acidogenesis) were successful, because the COD was converted into VFA. Also, the 60% methane concentration of the sequestered biogas showed that methanogenesis process was successful. The increasing VFA concentration and instability of the reactor, however, showed that the acetogenesis process was strongly inhibited.

When the Gebauer undiluted reactor observed results for methane production and VFA are compared to Lanari and Franci, the high sodium concentration could be blamed for the inhibition of acetogenesis and eventual failure of the reactor. But, when the Gebauer undiluted reactor observed values for methane production and VFA content are compared to those of Soto et al. (1991), Mendez et al. (1995), Omil et al. (1996) and Punal and Lema (1999) the high COD concentration could be noted as the reason for inhibition.

As previously stated it can be difficult to draw any conclusions comparing one research project to another due to eminent differences in design conditions, sludge characteristics and reactor type. But, by comparing a variety of research projects addressing each condition (ammonia and sulphate levels; COD loading rate and concentration; sodium concentration), safe and general conclusions can be made. The conclusion that can be drawn from examining and comparing the above data is that high saline environments increase the chances of failure by overloading in an anaerobic digester. The failure occurs due to a decrease in contact between the methanogenic bacteria and available COD and an increase in contact between the methanogenic bacteria and sodium. The contact dynamic has a higher impact on the acetogenesis process than any other step in the anaerobic digestion process which was proven by the unstable and increasing values of VFA in the failed Gebauer reactor.

The previous conclusion can have a large impact on large scale wastewater treatment of sludge drawn from high saline environments. The Soto et al. (1991), Mendez et al. (1995), Omil et al. (1996) and Punal and Lema (1999) studies suggest that the maximum treatable COD for an ocean water sludge, which can be assumed to consist of 10.2 g Na/l, is approximately 17-35 g COD/l of sludge. The net energy generation potential for harnessing the biogas was reported as 80-165 MW h/year (Gebauer 166). The COD limit conclusion can have a large effect on the economic efficiency of treatment of fish sludge onsite at offshore fish farms, because in order to treat a high COD concentration, high saline sludge a 1:1 dilution with tap water may be necessary. The environmental and economic costs of the 1:1 tap water dilution rate may outweigh any benefit of avoiding shipping the sludge to an onshore wastewater treatment facility for stabilization. The heat required to bring the tap water to mesophilic conditions may also outweigh the benefit of harnessing the sequestered methane for energy generation.

References:

Ciborowski, P., “Anaerobic Digestion in the Dairy Industry”, Minnesota Pollution Control Agency Air Innovations Conference, 2004, www.epa.gov. Accessed 18 Nov 2007.

Gebauer, Ruth. “Mesophilic Anaerobic Treatment of Sludge from Saline Fish Farm Effluents with Biogas Production.” Bioresource Technology, 2004, pages 155-167. Accessed 27 Nov 2007.

Thauer, R. K., "Biochemistry of Methanogenesis: a Tribute to Marjory Stephenson." Microbiology, 1998, volume 144, pages 2377-2406. Accessed 18 Nov 2007.

Lanari, D., Franci, C., “Biogas Production from Solid Wastes Removed from Fish Farm Effluents.” Aquatic Living Resources, 1998, pages 289-295. Accessed 19 Nov 2007.

Kugelman, I.J., Van Gorder, S., 1991. “Water and Energy Recycling in Closed Aquatic Systems.” Engineering Aspects of Intensive Aquaculture. Cornell University Aquaculture Symposium, April 1991. Accessed 20 Nov 2007.

McCarty, P.L., 1964. Anaerobic waste treatment fundamentals, part III: Toxic materials and their control. Public Works 95 (11), 91–94.

Melbinger, N.R., Donellon, J., 1971. Toxic effects of ammonia nitrogen in high-rate digestion. Journal Water Pollution Federation 43 (6), 1658–1670. Accessed 27 Nov 2007

Koster, I.W., Lettinga, G., 1988. Anaerobic digestion at extreme ammonia concentrations. Biological Wastes 25 (1), 51–59. Accessed 27 Nov 2007

Soto, M., Mendez, R., Lema, J.M., 1991. Biodegradability and toxicity in the anaerobic treatment of fish canning wastewaters. Environmental Technology 12, 669–677. Accessed 27 Nov 2007

Mendez, R., Lema, J.M., Soto, M., 1995. Treatment of seafood processing wastewaters in mesophilic and thermophilic anaerobic filters. Water Environment Research 67 (1), 33–45. Accessed 27 Nov 2007

Omil, F., Mendez, R., Lema, J.M., 1996. Anaerobic treatment of seafood processing waste waters in an industrial anaerobic pilot plant. Water SA 22 (2), 173–181. Accessed 27 Nov 2007

Punal, A., Lema, J.M., 1999. Anaerobic treatment of wastewater from a fish-canning factory in a full-scale upflow anaerobic sludge blanket (UASB) reactor. Water Science and Technology 40 (8), 57–62. Accessed 27 Nov 2007