Sludge Blanket Anaerobic membrane bioreactor (SB-AnMBR) Treatment of Prehydrolysis Liquor from the Dissolving Pulp Industry

Mayur M Kale[1], Kripa S Singh[1,*]

[1]*Dept. of Civil Engineering University of New Brunswick, NB, Canada.*
*Email: singhk@unb.ca

Abstract

Performance of innovative sludge-blanket anaerobic membrane bioreactors (SB-AnMBRs) was evaluated at mesophilic (35 ^{o}C for 400 days) followed by thermophilic (55 ^{o}C for 330 days) temperatures for the treatment of the pre-hydrolysis liquor (PHL) waste stream from a dissolving pulp production plant. PHL with an average total chemical oxygen demand (COD) of 100 g/L was generated from the steam hydrolysis of wood and mainly consisted of sugars (hemicelluloses), acetic acid, furfural and lignin. The bioreactors were fed with PHL at organic loading rates (OLR) ranging from 0.8 to 7.5 kg-COD/m^3-d to study the performance with respect to the COD removal, methane (bio-energy) production, effluent characteristics, and membrane fouling. Average COD removal of 91% and specific methane yield of 0.36 m^3/kg-COD$_{removed}$/day were achieved during the pseudo-steady period of the continuous mesophilic operation at each loading rate. The effluent lignin concentration showed an increasing trend (0.2 g/l to 2.7 g/l) with an increase in the OLR. At thermophilic condition, the AnMBR exhibited accumulation of volatile fatty acid (VFAs), the presence of slow-degrading lignin in the effluent and lower COD removals (less than 60%) possibly due to the one-step increase in the temperature (from 35 to 55 ^{o}C) exerting temperature stress on biomass during the first sixty days of the operation. Subsequently, it was observed that the methane yield slowly increased to 0.38 m^3/kg-COD$_{removed}$/day. This phenomenon can be ascribed to the shift in the population increase of thermophilic anaerobic bacteria. There was no sugar and furfural found in the effluent of the SB-AnMBR at both temperatures during the stable period. This suggested good potential of using the AnMBRs for the treatment of PHL as well as production of bio-energy. Flat-sheet membranes were used in the SB-AnMBRs. Membranes did not show significant fouling based on monitoring of temporal variations in the trans-membrane pressure at a sustained flux of 0.1 m^3/m^2/d during the aprox. 700 days of the continuous operation.

Keywords: pre-hydrolysed liquor; SB-AnMBR; lignin.

Introduction

Pre-hydrolyzed is one of the important steps in pulping process of wood in rayon production. Direct steaming (@ 150-170 ^{0}C) is utilized for pre-hydrolysis, which releases organic acids and hydrolyses hemicelluloses into reducing sugars. The spent liquid is known as pre-hydrolysis liquor (PHL), a waste product which is considered for this study.

The presence of acetic acid generated by the cleavage of acetyl groups decreases the pH, facilitating the removal of hemicelluloses. Few steps in the pre-hydrolysis process are the depolymerisation and dissolution of hemicelluloses which results in the formation of sugars (oligomers). High temperature treatment helps in removal of hexose and pentose sugars from PHL. Thus PHL constituting organics (which includes carbohydrates, acetic acid, lignin and sugar-decomposition products such as furfural) with chemical oxygen demand close to 100 g/L presents a considerable disposal problem for the dissolving pulp manufacturing industry. Currently an energy intensive process of evaporation and use of recovery boilers are used for the disposal of the PHL.

The development and progress of anaerobic treatment, applied for the treatment of industrial wastewaters universally is largely due to the development of high-rate bioreactors (Lettinga et al., 1995). One such variation in anaerobic technology is of membrane technology which allows biomass retention capability through the effective separation of solid retention time from hydraulic retention time, allowing for high loads. Essential biomass consortia are retained by the help of microfiltration assisting in the process of acclimation.

Mesophilic temperatures regimes (30-40^{0}C) have long been used for anaerobic digestion and had shown good operational performance. Thermophilic treatment can be useful for high temperature waste stream from industries. Processes like thermo-mechanical pulping or pre-hydrolysis use a high temperature for the treatment of wood. Thermophilic anaerobic treatment efficiency of 60-80% at high organic loading rates (1.07 to 12.25 kg-COD/m^3/d) for high temperature wastewater has been verified through various research (Duran and Speece, 1997; Rintala et al., 1992). Studies have also showed anaerobic treatability of pulp paper effluents at around 55^{o}C with removal efficiency obtained around 60-80% at higher loading rate (1.2 Kg COD/m^3/day) (Saikinoja-Salonen et al., 1983). Moreover, thermophilic treatment can also obviate the cooling of wastewaters and would allow treated water to be disposed safely.

One of the disadvantages of working with a thermophilic reactor is the unavailability of the thermophilic seed sludge for start-ups. Thus, mesophilic sludge was used as a seed for the start-up of the thermophilic reactor in this study. The transition from mesophilic to thermophilic temperatures is one of the concerns while adapting mesophilic seed sludge for thermophilic reactor as acclimatization would require long retention time. Two strategies are popularly used: the one-step (Syutsubo et al. 1997 and Van Lier et al., 1992) or the step-wise (Zabranska et al., 2002) temperature increase process. Bouskova et al., (2005) observed that the one-step temperature increase has proved to be a much faster strategy than the gradual increase of the reactor temperature. They also suggested that for each step of increase, the bacteria take time to acclimatize and to regain their efficiency. Thus the overall time required for start-up (i.e from 35^{o}C to 55^{o}C) is less in the one-step process as compared to the gradual increase strategy (Bouskova et al., 2005). Thus, the one-step increase, from 35 ^{0}C to 55^{0}C, start-up method was adopted for this study.

The purpose of this study is to evaluate the technical feasibility of modified submerged sludge-bed AnMBR operating under mesophilic (35^{0}C) and thermophilic (55^{0}C) conditions with respect to performance, quality of effluent and potential of value-added by-product (biogas) recovery.

Materials and methods

Figure 1 shows a schematic of an experimental setup of a stainless steel 50L lab-scale SB-AnMBR, designed to have a membrane module submerged in the top portion, while the bottom portion consist of a sludge bed.

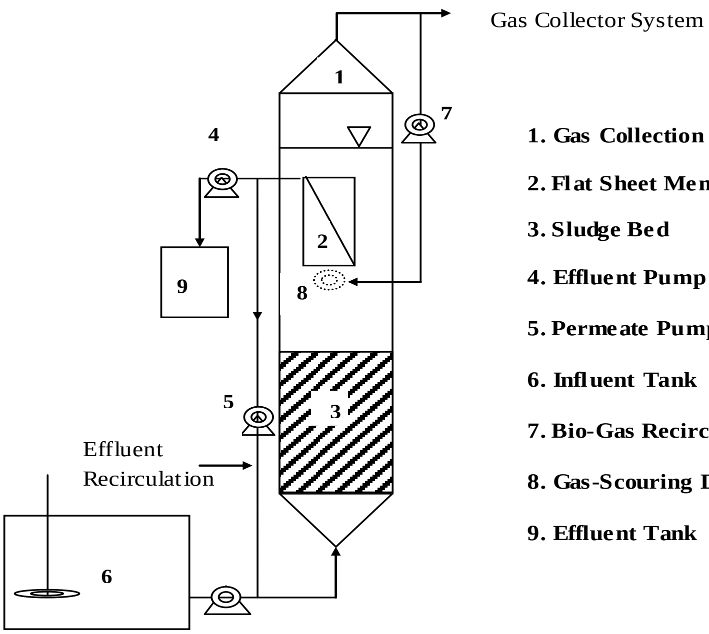

Figure 1. Schematic diagram for experimental setup

Mesophilic SB-AnMBR (35^{0}C) and thermophilic SB-AnMBR (55^{0}C) semi pilot-scale reactors were operated to treat the PHL at a series of organic loading rates (OLR) of 0.8 to 7.5 kg-COD/m^3/d. The temperature of the reactors was controlled by the thermo coil wrapped around the outer body of the reactor. The mesophilic SB-AnMBR was seeded with the granular sludge obtained from an anaerobic reactor (35^{0}C) with specific methanogenic activity 0.33 gCOD/gVSS/d. After completion of the experimental cycle for mesophilic stage, the temperature of mesophilic SB-AnMBR reactor was increased in a single step to achieve thermophilic temperature (from 35 ^{0}C to 55 ^{0}C). This instance was considered as day zero for thermophilic reactor. Thermophilic SB-AnMBR was operated to treat the PHL at a series of organic loading rates (OLR) of 0.8 to 7.5 kg-COD/m^3/d.

Biogas was recirculated using a diffuser which was placed above the sludge bed. This helped in the scouring of three chlorinated polyethylene flat sheet microfiltration Kubota membranes (Type 203, Japan, the surface area of each membrane was 0.11 m^2, and the nominal pore size was 0.4 μm) to reduce fouling as well as to allow sufficient mixing in the reactor. Wastewater (PHL) was fed from the bottom portion of the reactor and effluent and permeate were filtered through the membranes to achieve a flux of 0.1 m^3/m^2/d. Permeate was recycled continuously.

The PHL was obtained from a dissolving pulp facility situated in New Brunswick, Canada. SB-AnMBR influent and effluent were analysed for COD, biochemical oxygen demand (BOD_5), solid content (total, dissolved and volatile solids) and carbon content, following the Standard Methods (A.P.H.A, 2005). Organic constituents such as acetic acid, furfural, carbohydrates, and lignin were analyzed using NMR (Varian/Agilent UNITY INOVA NMR-300 spectrometer, USA), ion chromatograph unit mounted with CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD), and UV spectrometric method using Genesys 6 UV spectrophotometer (Thermo Electron Corporation, Madison, WI, USA) at the wavelength of 205 nm. The biogas samples were analyzed for methane, carbon dioxide, oxygen, and nitrogen in a Varian CP 3800 gas chromatograph (Varian Inc., USA).

PHL characterization

The average COD value of the PHL was around 100 g/L with a BOD_5 value of 55 g/L. The low BOD_5/COD ratio can be attributed to the presence of refractory components of the PHL which are not represented by BOD_5 (Speece 1996). Characterization of the PHL showed that it contained pentose and hexose carbohydrates as monomeric (14.5 g/L) and oligomeric (39.7 g/L) forms along with acetic acid (10.4 g/L), furfural (1.14 g/L) and lignin (11 g/L) (Table 1). The effect of loading on the degradation of the PHL in anaerobic conditions at 35^0C and 55^0C was studied by Debnath et al. (2013). They concluded from their respirometric batch studies that the reactor efficiency decreased with the increase in the PHL concentration. This can be attributed to increasing the concentration of slow anaerobically biodegradable components of PHL such as dissolved lignin.

Table 1. Characteristics of PHL

Parameters	**pH**	**COD, g/L (% soluble COD)**	**BOD_5, g/L (% soluble BOD)**	**Total solids, g/L (%TDS)**
Values	3.4-4	100 (90 %)	55 (88 %)	121 (96 %)
Parameters	**Acetic acid**	**Furfural**	**Lignin**	**Sugars**
Values	10.4 g/L	1.1 g/L	11 g/L	54.2 g/L

They also reported a 70% decrease in the efficiency of methane production with the one-step increase in the temperature from 35 ^{0}C to 55 ^{0}C which might be due to temperature shock. The influent (PHL) with 100 g/L of COD could not be fed directly to the reactor, as the substrate inhibition would adversely affect the reaction rate. Thus, the PHL was diluted to achieve COD conc. of 20 g/L and 50 g/L, and the OLR applied ranged from 0.8 to 7.5 kg-COD/m^3/d.

Experimental design

The PHL was diluted to achieve the organic loading rates (OLRs) of 0.8, 1.2 and 2 kg-COD/m^3.d at COD of 20 g/L; 2, 3 and 5 kg-COD/m^3.d at COD of 50 g/L and 5, 7.5. In order to evaluate the interactive effects of hydraulic retention time (HRT) and $COD_{influent}$ on the performance indicators in a continuous reactor, eight continuous experiments were conducted. Details of the experimental design are presented in Table 2.

Table 2. Experimental design of mesophilic and thermophilic studies.

Runs	Temp. (^{0}C)	HRT (Days)	OLR (kg-COD/m^3/day)	COD$_{(influent)}$ (g/L)	Performance indicators
1	35^{0}C & 55^{0}C	25	0.8	20	1. Effluent(COD,BOD,TOC) and volatile fatty acids, 2. Biogas composition, 3. methane production rate, 4. Solids content:Total, dissolved and volatile solids 5. pH, oxidation retention potential (ORP) and alkalinity.
2		16.7	1.2		
3		10	2		
4		25	2	50	
5		16.7	3		
6		10	5		
7		25	5	100	
8		16.7	7.5		

Results and Discussion

The reactor performance, membrane performance and sludge characteristics were studied to evaluate the capacity of SB-AnMBR to sustain the applied organic loadings. Effluent quality was the primary indicator for reactor performance. Effluent COD concentrations and COD removal efficiency were analyzed. Mesophilic SB-AnMBR showed an average of more than 85% removal efficiency for COD irrespective of the variation in the OLR (Figure 2). The effluent BOD increased from an average of 0.22 to 2.54 g/L with increase in OLR with corresponding BOD removal of greater than 95% throughout the study period. This suggests that most of the easily biodegradable substances present in the influent were degraded. It was also observed that the COD removal efficiency was not affected by the change in influent COD from 20 g/L to 50 g/L or from 50 g/L to 100 g/L at steady state conditions. These results are similar but superior to the results from the study presented by Rao et al. (2006) working with an upflow anaerobic sludge blanket (UASB) treating similar wastewater at organic loading rates ranging from 1 to 7.5 kg-COD/m^3/d. They reported that the UASB reactor could achieve 70–75% of COD removal efficiency and 85–90% BOD removal efficiency while treating PHL.

Results from constitutional analysis of the effluent at mesophilic temperatures indicated almost complete degradation of sugars and acetic acid as well as furfural. The lignin in effluent increased from 0.2 to 3.26 g/L with an increase in the OLR. The effluent COD concentration varied in the range of 1.0-13.2 g/L and mainly consisted of untreated dissolved lignin.

The temperature of SB-AnMBR was increased from 35 ^{0}C to 55 ^{0}C. A sudden drop in the COD (Figure 2), BOD, TOC and lignin removal efficiency was observed in the thermophilic SB-AnMBR with the temperature increase from 35^{0}C to 55 ^{0}C for the first 25 days. The initial lower total volatile acids were observed as 0.87 g/L in mesophilic reactor as compared to 2.15 g/L in the thermophilic condition. The effect of temperature causing slower hydrolysis in thermophilic conditions as compared to the mesophilic condition might be the reason behind the accumulation of VFAs. The higher VFA level in the thermophilic reactor in comparison to the mesophilic one was also reported by Song et al. (2004). Bouskova et al. (2005) reported a high VFA concentration in the effluent from thermophilic processes in comparison with the results obtained from mesophilic process. However, after around 30-40 days, the propionate concentration was not detected and the total VA/PA ratio of 0.17 was observed, which was well below of the value 0.8 indicating a stable process (Ripley et al,1986).

After the bacteria acclimatized to the temperature shock from 35^{0}C to 55^{0}C, the reactor showed better performance with average COD removal of more than 90% at the pseudo steady state (Figure 2). At the pseudo steady state, the results from NMR and sugar analysis indicated that the sugars, acetic acid as well as the furfural were almost completely degraded by anaerobic bacteria.

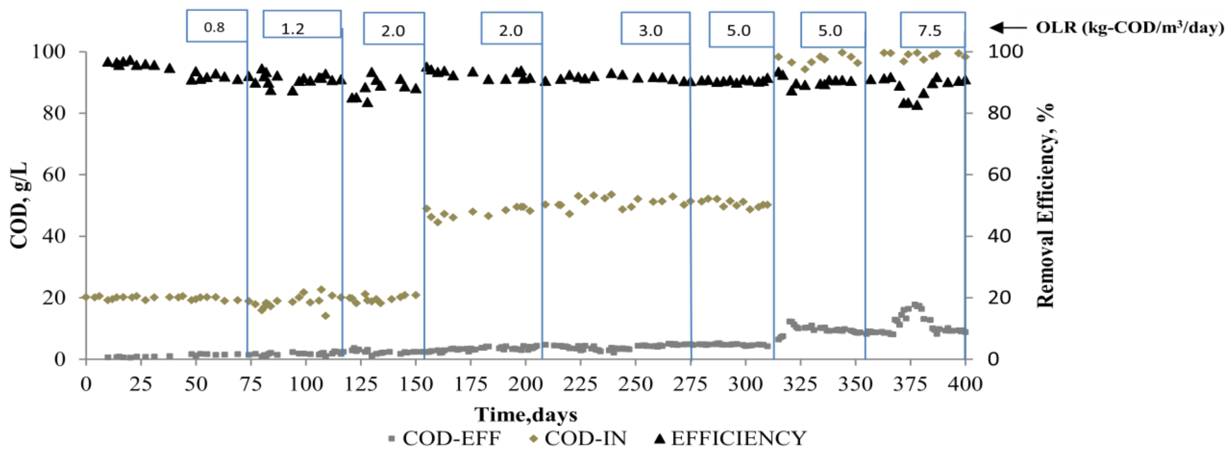

Figure 2. Mesophilic SB-AnMBR: COD concentration and removal

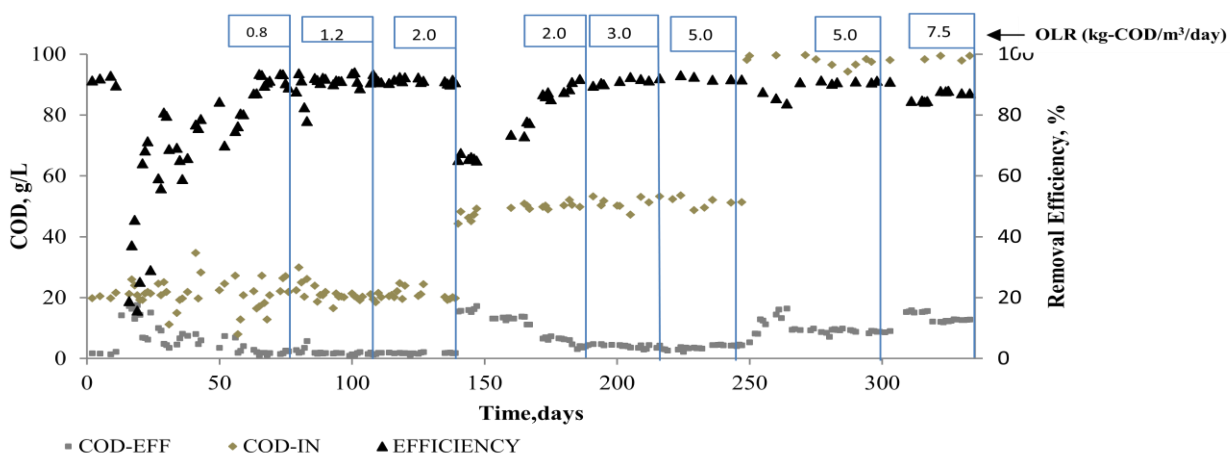

Figure 3. Thermophilic SB-AnMBR: COD concentration and removal

Another reason for initial lower COD removal efficiency and residual high effluent COD after achieving the pseudo steady state in the thermophilic reactor and mesophilic reactor might be due to the slow biodegradation of lignin (efficiency= 50-80% for OLR ranging from 0.8 to 7.5 kg-COD/m^3/d). The absence of depolymerizing enzymes or any other oxidizing agent in higher molecular weight of lignin is another reason behind its low biodegradability and refractory nature. Toxicity due to the presence of higher concentration of lignin can also hamper the biodegradability (Sierra-Alvarez and Lattinga 1991). This can be ascribed to the reduction in the removal efficiency of COD and lignin with increase in the OLR.

In order to evaluate the performance, the specific methane yield from the reactor was calculated (Table 3). Methane production observed during the experimental cycle was converted to COD using ideal rate of methane production (Speece, 1996). Methane content was 50-55 % of the total biogas with CO_2 representing 38-45 % in mesophilic reactor. During pseudo-steady phases of the operation of mesophilic reactor the rate of methane production was in the rage of 0.33 to 0.39 m^3-CH_4/kg-$COD_{(removed)}$/d for OLR from 0.8 to 7.5 kg-COD/m^3/d, which is comparable to the theoretical value of 0.395 m^3-CH_4/kg-$COD_{(removed)}$/d at 35^0C and 1 atm (Table 3).

Table 3. SB-AnMBR COD balance results.

OLR (kg-COD/ m^3/day)	Mesophilic reactor		Thermophilic reactor	
	COD converted to biogas (%)	Rate of methane prod. (m^3-CH_4/kg-COD $_{(removed)}$/ d)	COD converted to biogas (%)	Rate of methane prod. (m^3-CH_4/kg-COD $_{(removed)}$/ d)
0.8	91.26	0.39	84.84	0.41
1.2	81.06	0.35	88.35	0.42
2	78.03	0.33	84.37	0.39
2	86.18	0.37	89.54	0.41
3	83.00	0.36	87.28	0.39
5	83.02	0.36	79.54	0.37
5	82.72	0.36	88.72	0.41
7.5	80.40	0.35	74.70	0.36

Throughout the pseudo-steady phase of operation of the thermophilic reactor the average rate of methane production was 0.38 m^3CH_4/kg.$COD_{removal}$/d for OLR 0.8 to 7.5 kg-COD/m^3/d (Table 4). These results are comparable to the theoretical value of 0.42 m^3/kg.$COD_{removal}$/d at 55 ^{0}C and 1 atm (Speece, 1996). Thus, PHL was readily converted to methane and SB-AnMBR can efficiently treat a high strength PHL stream at both temperatures. The biogas composition responded to the temperature increase by a significant decrease and reached the minimum level of 20% of methane in the biogas after increasing the temperature to 55 ^{0}C in one-step. The methane content increased again after day 30 and stabilized, slightly fluctuating around the value of 60% of methane in the biogas. After 60 days, the biogas production was considered stable. Higher methane content and yield might be ascribed to the presence of thermophiles in the mesophilic inoculum. They also might have assisted in fast adaptation and facilitated the predominance of thermophilic bacterial population in the reactor (Chen, 1983 and Boušková et al. 2005).

The idea behind increasing the temperature of the mesophilic reactor acclimatized to a high organic load of the PHL was to limit the effect of slow biodegradable components on the efficiency of the reactor. The rational was that with the increase in concentration of the PHL in the feed, the amounts of slow biodegradable substrates (e.g. lignin and furfural) will also increase. The increase in methane conversion efficiency with acclimatization can be explained due to the presence of the small percentage of thermophiles in mesophilic sludge. They may serve as a foundation for the rapid development of the thermophilic bacterial population as they have higher growth rate (Chen, 1983). Chachkhiani et al. (2004) also concluded from their observations that thermophiles already present in the inoculum takes part in the anaerobic thermophilic conditions.

It is also evident from the above table that though the anaerobes were sufficiently acclimatized at 55 ^{0}C, still increase in organic concentration can easily affect the methane conversion rate (19% decrease).

Membrane performance

The SB-AnMBR was operated at constant flux of 0.1 $m^3/m^2/d$ for 400 days (Figure 4). The effect of the increase in flux was observed throughout the experiment. Membranes are considered to be fouled and require a cleaning when the TMP exceeded 40 inches of water or if the membranes were ineffective in producing the permeate. Scouring through the recirculation of biogas was helpful in reducing membrane fouling. In addition to scouring, SB-AnMBR was designed to have a sludge bed zone at the bottom portion and relatively dispersed sludge at the top portion of the reactor. Results showed a difference in the average mixed liquor suspended solids content at the top portion (40g/L) and at the bottom portion (60 g/L) of the reactor which might have helped in reducing the fouling. During the first 200 days of operation of mesophilic reactor at 0.1 $m^3/m^2/d$, the TMP was well below 15 inches of water. Beyond this point the membranes were taken out for cleaning as it was observed that there was no production of permeate. Deposition of colloids reduced the pores of the cake layer to the extent that permeate could not be withdrawn (Drews, 2010). Though the TMP gauge did not record TMP above 40 inches of water, still it was necessary to clean or replace the membrane to ensure continuous flow of the permeate.

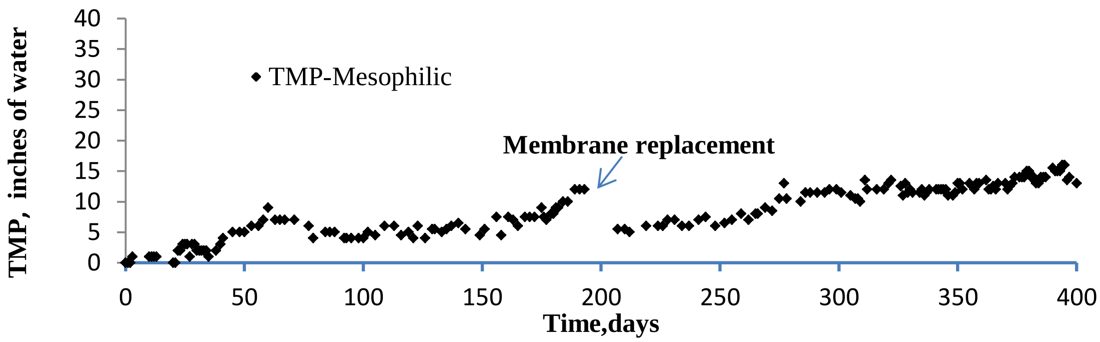

Figure 4. Variation of TMP of mesophilic reactor with respect to time.

The thermophilic SB-AnMBRs was also operated at a constant flux of 0.1 $m^3/m^2/d$ throughout the study (Figure 5). During the first 278 days of experimental cycle the TMP was well below 20 inches of water in the thermophilic reactor. The sudden increase in TMP (33 inches of water) and no effluent collection after around 280 days, indicated that the membranes were fouled and needed cleaning. At this point the membrane were taken out and replaced to continue the operation.

This demonstrates that the SB-AnMBR can be operated under mesophilic and thermophilic conditions without significant membrane fouling at the loading and flux that was applied.

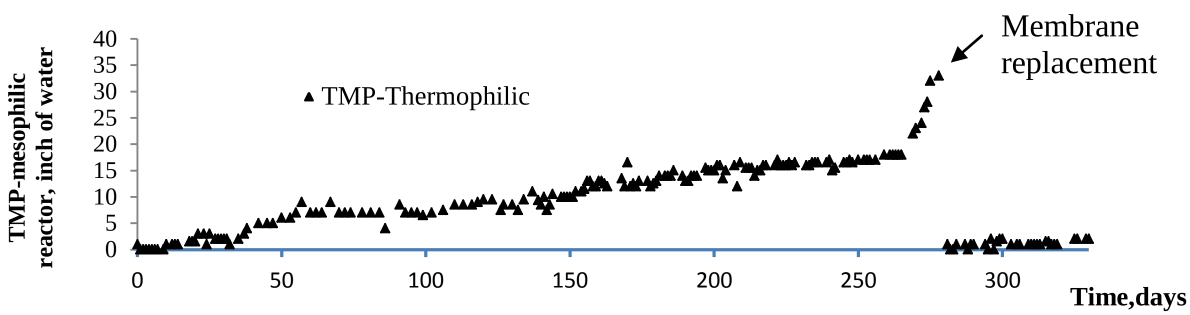

Figure 5. Variation of TMP of thermophilic reactor with respect to time.

Conclusion

To our knowledge, SB-AnMBR application particularly for the PHL from Canadian pulp industry has not been studied previously. Overall results indicated that the mesophilic and thermophilic reactor showed distinct advantage in terms of average removal of COD and BOD more than 85% and quantity and quality of biogas production(methane yield: more than 0.33 m^3-CH_4/kg-COD $_{(removed)}$/ d). Acetic acid and furfural were almost completely degraded. Moreover, 60-80 % of lignin was also successfully removed from the waste stream. It is possible to replace the current PHL disposal method (evaporation and use of recovery boiler) with SB-AnMBR systems but would require a further investigation into its economics and technical feasibility at the pilot scale operation.

Acknowledgements

The authors would like to acknowledge the funding agencies including the Atlantic Canada Opportunity Agency (ACOA) under the *Atlantic Innovation Fund (AIF) program*, the Natural Science and Engineering Research Council (NSERC), the New Brunswick Innovation Foundation (NBIF) and ADI Systems Inc. Dr. Dennis Connor, Jangchuk Tashi and Dibyendu Debnath are acknowledged for their technical support during the study.

References

A.P.H.A., A.W.W.A., W.E.F. *(2005),* Standard Methods for the Examination of Water and Wastewater. 21st edn, American Public Health Association/American Water Works

Boušková, A., Dohányos, M., Schmidt, J. E., and Angelidaki, I. 2005. Strategies for changing temperature from mesophilic to thermophilic conditions in anaerobic CSTR reactors treating sewage sludge. Water Res., 39(8): 1481-1488.

Chachkhiani, M., Dabert, P., Abzianidze, T., Partskhaladze,G., Tsiklauri, L., Dudauri, T., Godon, J.J. 2004. 16S rDNA charcterisation of bacterial and archaeal communitiesduring start-up of anaerobic thermophilic digestion of cattle manure. Bioresource Technol. 93: 227–232.

Chen, M. 1983 Adaptation of mesophilic anaerobic sewage fermentor population to thermophilic temperatures. *Appl. Environ. Microbiol.* 45: 1271–1276.

Debnath D, Kale M and Singh K. (2013). Characterization and anaerobic treatability study of pre-hydrolysis liquor (PHL) from dissolving pulp mill. *Water Quality Research Journal of Canada*. 48(2), 145–154.

Duran, M. and Speece, R. 1997. Temperature staged anaerobic processes. Environ. Technol. 18: 747±754.

Lettinga, G. 1995. Anaerobic digestion and wastewater treatment systems. Antonie Van Leeuwenhoek Int.J.Gen.Mol.Microbiol., 67(1): 3-28.

Rao,G., Bapat, A. 2006. Anaerobic treatment of pre-hydrolysate liquor (PHL) from a rayon grade mill: pilot and full scale experience with UASB reactors. Biores. Technol., 97: 2311–2320.

Rintala, J. and Lepisto, S. 1992. Anaerobic treatment of thermomechanical pulping whitewater at 35-70°C. Water Res., 26(10): 1297-1305.

Ripley, L., Boyle, W., Converse, J. 1986. Improved alkalimetric monitoring for anaerobic digestion of high-strength wastes. Journal Water Pollution Control Federation, 58 (5), 406-411.

Salkinoja-Salonen M., Valo R. and Apajalahti J., (1983). “Treatment of pulp and paper wastewaters in an anaerobic reactor: from bench size units to full scale operation.” *Proceedings Third Int. Symp. On Anaerobic Digestion* Boston, Mass., 107–121.

Sierra-Alvarez R. and Lettinga G. 1991. The methanogenic toxicity of wastewater lignins and lignin related compounds. J Chem Tech Biotechnol. 50: 443-455.

Song, Y.-Ch., Kwon, S.-J., Woo, J.-H. (2004) Mesophilic andthermophilic co-phase anaerobic digestion compared withsingle-stage mesophilic- and thermophilic digestion ofsewage sludge. Water Res. 38: 1653–1662.

Speece, R. (1996) Anaerobic Biotechnology for Industrial Wastewaters, Archae Press: Nashville, Tennesesse.

Standard Methods for the Examination of Water and Wastewater (2005) 21st edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Syutsubo, K., Harada, H., Ohashi, A., Suzuki, H. (1997). “An effective start-up of thermophilic UASB reactor by seeding mesophically-grown granular sludge.” *Water Sci. Tech.*, 36 (6–7),391–398.

Van Lier J., Grolle K., Stams A., de Maccario E. and Lettinga G.(1992) “Start-up of a thermophilic upflow anaerobic sludge bed (UASB) reactor with mesophilic granular sludge”, *Appl. Microbiol. Biotechnol.* 37, pp. 130–135.

Zábranská, J., Dohányos, M., Jeníček, P., Zaplatílková, P., and Kutil, J. (2002). “The contribution of thermophilic anaerobic digestion to the stable operation of wastewater sludge treatment.” *Water Sci. Technol.*, 46(4-5), 447-453.