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A NOVEL SLUDGE-BED ANAEROBIC MEMBRANE BIOREACTOR FOR SUSTAINABLE TREATMENT OF INDUSTRIAL WASTEWATER

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ABSTRACT

Dissolving pulp mill wastewater called prehydrolysis liquor (PHL) obtained from steam (at 150-170^{0}C) treatment of wood had a total chemical oxygen demand (COD) of approximately 100 g/L contains mainly sugars, furfural, lignin, and acetic acid, poses a considerable wastewater disposal problem. Replacement of the current energy intensive disposal method (evaporation and use of recovery boiler) is a requirement of dissolving pulp industry. The bioreactors were fed with PHL at organic loading rates (OLR) ranging from 0.8 to 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. Whereas, in thermophilic conditions, a methane yield of 0.38 m^3/kg-COD$_{removed}$/day was observed. There was no sugar and furfural found in the effluent of the SB-AnMBR at both temperatures (35^{0}C and 55^{0}C) during the pseudo-steady period. High effluent COD can be attributed to lignin in the effluent (0.2 to 1.6 g/L). Flat-sheet membranes used in the SB-AnMBRs 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 550 days of the continuous operation.

Keywords: pre-hydrolysed liquor; SB-AnMBR; lignin; methane production; fouling.

1. INTRODUCTION

Anaerobic processes have become popular for industries to manage their high strength waste streams and generate bio-energy. Anaerobic biotechnology can be preferred for treatment of high strength wastewaters as it converts waste to an energy rich by-product (methane rich biogas), suitable for energy production and generates low amounts of waste sludge, as compared to aerobic treatment options. Though biological treatment options have been extensively researched and applied for industrial and municipal wastewater treatment, they still have limitations and challenges, which inspire researchers to develop the next generation of sustainable and green high-rate anaerobic bioreactor technologies (Metcalf & Eddy, 2006).

The use of membranes with bioreactors is a recent development in the area of industrial wastewater treatment technology (Liao et al., 2006). Membrane bioreactors are one of most recent modifications evolved to optimize biological processes which ensure biomass retention by the application of microfiltration processes. This allows operation at high sludge concentrations (Stephenson, 2000). It is an attractive option for waste stabilization. One of the main advantages of membrane bioreactors is that the filtration process in the bioreactor enables the production of a superior quality effluent.

This study involves the treatment of a waste stream effluent from a pulp mill producing “dissolving pulp” using an anaerobic membrane reactor. The wood pulp is the main raw material used in the manufacture of a viscose staple fibre (Rayon). The pre-hydrolysis step is introduced prior to the kraft pulping process in order to increase the cellulose content. In the pre-hydrolysis step, wood is treated with steam (150-170ºC) to remove hemicellulose. This produces a pre-hydrolyzed condensate or pre-hydrolysis liquor (PHL) which is a waste product mainly consisting of carbohydrates. The high temperature of the waste stream can be utilized for thermophilic digestion. The increase in the reactor temperature may enhance the reaction rate and thus improve the efficiency of degradation.

The PHL is presently being evaporated and burned in the recovery boiler which is an energy intensive process. So, the industries are looking for an alternative disposal methods which can be efficient and effective. Anaerobic membrane reactors are considered suitable bioreactor for the treatment of high strength wastewater such as PHL and membranes can maintain active sludge in the reactor enhancing the degradation process (Liao et al., 2006). Combining these two concepts can increase the effluent quality. A thermophilic operation would be considered to capitalize on the heat energy present in the waste stream. Thermophilic conditions can also improve the biogas quality and its production (Saikinoja-Salonen et al., 1983). The main objective of this paper is to evaluate the feasibility of using a novel AnMBR for the treatment PHL stream of the dissolving pulp mill. This study will offer industries an alternative treatment technology for safe disposal of waste and will also benefit them in offsetting the cost of energy through bio-energy production.

2. MATERIALS AND METHODS

The semi pilot-scale (total volume of 50 liters) mesophilic SB-AnMBR (35^0C) and thermophilic SB-AnMBR (55^0C) bioreactors were operated to treat the PHL at a series of organic loading rates (OLRs) ranging from 0.8 to 5 kg-COD/m^3/d (Figure 1). The mesophilic SB-AnMBR was seeded with the granular sludge obtained from an anaerobic reactor (35 ^{0}C) with specific methanogenic activity of 0.33 gCOD/gVSS/d. The temperature of the reactors was controlled by the thermo coil wrapped around the outer body of the reactor. After completion of experimental cycle for mesophilic stage, the temperature of mesophilic SB-AnMBR reactor was increased in a single step to achieve thermophilic temperature (from 35^0C to 55^0C). This instance was considered as day zero for the thermophilic reactor. SB-AnMBR was designed to have membranes submerged in the top one-third portion while the bottom portion consisted of a sludge bed. PHL was obtained from a dissolving pulp industry, situated in New Brunswick, Canada. The PHL(influent) and effluent from the reactor were analysed for wastewater characteristics like chemical oxygen demand (COD), biochemical oxygen demand (BOD), solid content and carbon content following the standard methods (A.P.H.A., A.W.W.A., W.E.F., 2005). Organic constituents such as acetic acid, furfural, carbohydrates, and lignin were analysed with the help of NMR (Varian 300 NMR-spectrometer), ion chromatograph unit mounted with CarboPac^{TM} PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) (PAD settings were E1 ¼ 0.1 V, E2 ¼ 0.6V and E3 ¼ -0.8V) and UV spectrometric method using Genesys 6 UV spectrophotometer (Thermo Electron Corporation, Madison, WI, USA) at wavelength of 205 nm. The biogas samples were analyzed for methane, carbon dioxide, oxygen, and nitrogen in Varian CP 3800 gas chromatograph equipped with packed steel column (TCD detector at constant temperature of 180ºC, and Helium as a carrier gas at 30 ml/min flowrate was used). Samples were analyzed in duplicates or triplicates. The average of the values, standard deviation and relative standard deviation (%RSD) were calculated for all the analysis conducted.

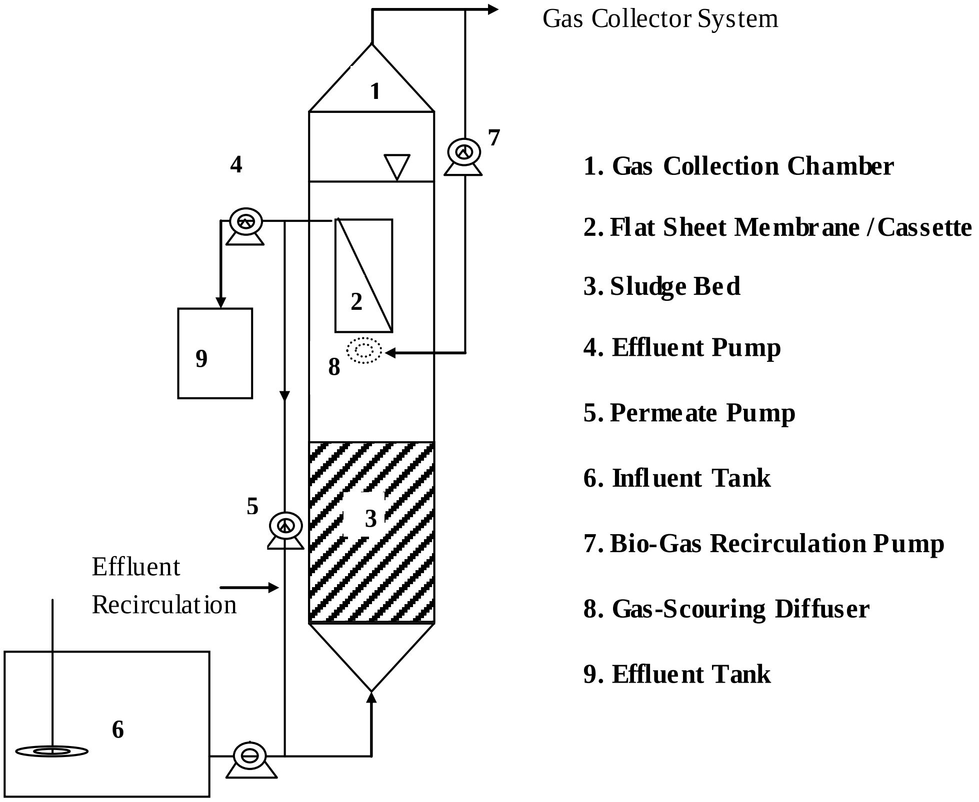

Figure 1: Schematic of experimental setup

The transmembrane pressure (TMP) was monitored with respect to time to evaluate the membrane performance. 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, Kubota, 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.

2.2 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 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). The effect of loading on the degradation of 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 an increase in PHL concentration. This can be attributed to increasing concentration of slow anaerobically biodegradable components of PHL such as dissolved lignin. Methane production with a one-step increase in the temperature from 35^0C to 55^0C indicated a 70% decrease in efficiency of the reactor which might be due to the 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 concentrations of 20 g/L and 50 g/L and the OLR applied ranged from 0.8 to 5 kg-COD/m^3/d.

Table 1: Characteristics of PHL

Parameters	**pH**	**COD, g/L (% soluble COD)**	**BOD_5, g/L (% soluble BOD)**	**Total volatile solids g/L (TDS)**
Values	3.4-4	100 (90 %)	55 (88 %)	94 (119)
%RSD	2.22	11.58	5.92	3.56
Parameters	**Acetic acid**	**Furfural**	**Lignin**	**Sugars**
Values	10.4 g/L	1.1 g/L	11 g/L	54.2 g/L
%RSD	1.05	1.14	4.58	2.58

3. RESULTS AND DISCUSSION

3.1 Reactor performance

The factors like OLR, hydraulic retention time (HRT), and influent COD in the experimental design for this study were kept almost identical as the study was intended to compare the performance of both types of reactors (Table 2). In order to observe the performance, the specific methane yields from both reactors were calculated.

Table 2: Experimental Design

Runs	**Temp. (^{0}C)** {days of operation}	**HRT (Days)**	**$COD_{(influent)}$ (g/L)**	**OLR kg-COD/ m^3/d**	**Performance indicators**
1	35 {~300} ------ 55 {~250}	25	20	0.8	1. Effluent: COD, BOD_5, TOC, volatile fatty acids, pH, oxidation reduction potential and alkalinity. 2. Composition of biogas, 3. Methane production rate, 4. Mixed liquor solids.
2		16.7		1.2	
3		10		2	
4		25	50	2	
5		16.7		3	
6		10		5	

COD mass balances for the mesophilic and thermophilic reactors are presented in Tables 3 and 4. During the stable phase of operation of the mesophilic reactor, the average rate of methane production was 0.35 $m^3CH_4/kg.COD_{removed}/d$, whereas for the thermophilic reactor, the average rate of methane production was 0.40 $m^3CH_4/kg.COD_{removed}/d$ for 0.8 to 5 kg-COD/m^3/d. They are comparable to the theoretical value of 0.395 $m^3/kg.COD_{removal}/d$ at 35^{0}C and 0.42 $m^3/kg.COD_{removal}/d$ at 55^{0}C and 1 atm (Speece,1996). This indicates that the SB-AnMBR can efficiently treat a high strength PHL stream at both temperatures and anaerobes can efficiently convert constituents of PHL to methane. Methane content was 50-55 % of the total biogas with CO_2 representing 38-45 % in the mesophilic reactor. Whereas, the biogas composition responded to the temperature increment to 55 ^{0}C on day 11, by a significant decrease and reached the minimum level of 20% of methane in the biogas.

The methane content increased again after day 30 and stabilized 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 inocula. They also might have assisted in fast adaptation and served as a foundation for the development of thermophilic bacterial growth (Chen, 1983 and Boušková et al., 2005).

Table 3: Mass-balances on COD for the Mesophilic SB-AnMBR

OLR (kg-COD/ m^3 /d)	**Influent COD (g/day)**	**Effluent COD (g/day)**	**COD converted to methane (g/day)**	**Unaccounted COD (g/day)**
0.8	43	3.26	39.24	0.50
1.2	66.9	5.25	51.80	9.85
2	108.85	8.15	84.94	15.76
2	98.42	7.46	84.82	6.14
3	154.5	14.76	128.23	11.51
5	248.25	22.95	206.10	19.20

Note: Influent COD = Output COD + Unaccounted COD

Table 4: Mass-balances on COD for the Thermophilic SB-AnMBR

OLR (kg-COD/ m^3 /d)	**Influent COD (g/day)**	**Output COD**		**Unaccounted COD (g/day)**
		Effluent COD (g/day)	**COD converted to methane (g/day)**	
0.8	44.78	6.10	37.99	0.69
1.2	63.39	7.14	56.00	0.25
2	103.75	9.30	87.54	6.91
2	103.54	8.64	92.71	2.19
3	157.74	9.96	137.68	10.10
5	257.85	22.00	205.11	30.75

Note: Influent COD = Output COD + Unaccounted COD

The effluent quality of mesophilic SB-AnMBR indicated that an average of more than 90% removal efficiency for COD (Figure 2), BOD, and TOC at pseudo-steady state was observed irrespective of the change in OLR. The effluent COD concentration varied in a range of 1.0-5.0 g/L. These results are comparable but superior to the results reported (70–75% of COD removal efficiency for PHL treatment with UASB) in the study presented by Rao et al. (2006). The lignin in the effluent increased from an average 0.2 to 1.6 g/L in the mesophilic reactor. An average removal efficiency of lignin was found to be 77 % (Figure 3). It was suspected that the high effluent COD was mostly due to the presence of untreated dissolved lignin in the permeate of mesophilic SB-AnMBR.

As the thermophilic reactor was seeded with mesophilic sludge, the performance in terms of COD (Figure 3), BOD, TOC and lignin removal of the thermophilic SB-AnMBR was comparatively lower than that of the mesophilic SB-AnMBR for the first 60 days. But as the bacteria acclimatized to the temperature shock the reactor showed better performance with an average COD removal of more than 92% at pseudo steady state. Results from the NMR and sugar analysis indicated that the sugars, acetic acid as well as the furfural were almost completely degraded by anaerobic bacteria in the mesophilic and thermophilic reactors. VFAs were not observed in the mesophilic reactor. In the case of the thermophilic SB-AnMBR, the initial lower COD removal efficiency might be due to the accumulation of volatile fatty acids (VFAs). The acetic acid and propionic acid reached the highest concentration of 277.1 mg/L and 114 mg/L. Accumulation of these VFAs did not result in a system break down. The decomposition of acetic acid took place within the next 20-30 days. The decrease in propionate concentration occurred later than acetic acid concentration indicating a higher sensitivity of propionate degrading bacteria to a sudden temperature increase (Winther-Nielsen, 1991). The higher VFA level in the thermophilic reactor in comparison to the mesophilic reactor was also reported by Song et al. (2004).

The faster hydrolysis in comparison to the methanogenesis under thermophilic conditions might be the cause of an accumulation of VFAs. Another reason for the initial lower COD removal efficiency in the thermophilic reactor might be due to the slow biodegradation of lignin.

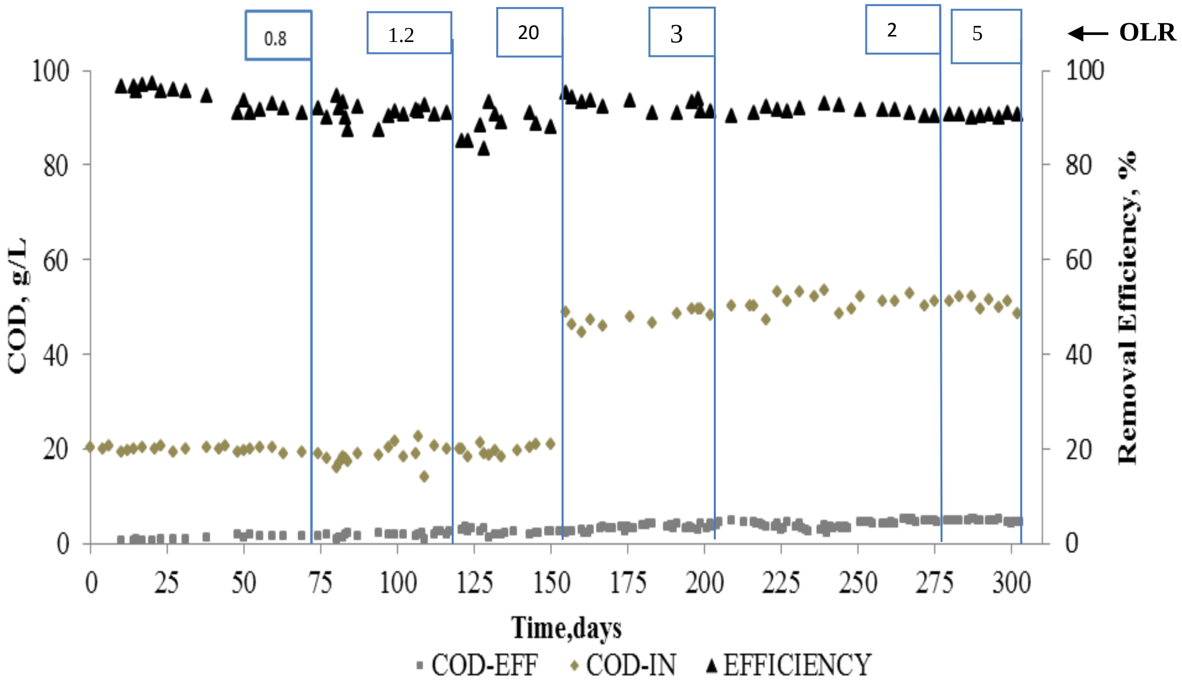

Figure 2: Mesophilic SB-AnMBR: COD concentration and removal efficiency

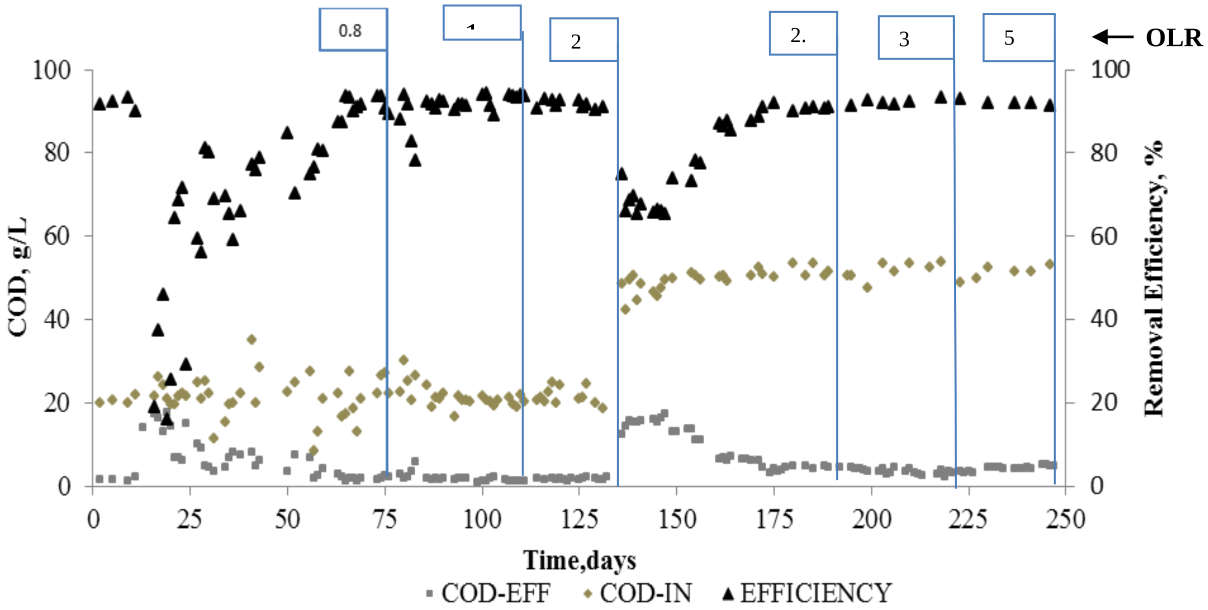

Figure 3: Thermophilic SB-AnMBR: COD concentration and removal efficiency

The lignin removal efficiency increased with an increase in the acclimatization time in the thermophilic reactor. A similar trend observed in the COD removal efficiency by Benner and Hodson (1985). They concluded that the rates of anaerobic biodegradation of high molecular weight lignin at 55^0C were 10-15 fold higher than reported at mesophilic temperatures. They also demonstrated that at high temperature, enhanced rates can convert the lignin and lignified substrates [kraft lignin (13–23%)] by anaerobic degradation to methane and low molecular-weight aromatic compounds. Complete degradation of lignin was not achieved in this study due to the toxicity effect, size of molecule and higher molecular weight of lignin which can be detrimental to anaerobes. Lignin is defined as a 600-1000 kDa molecule, which is too big to enter cell membranes (Kirk and Farrell 1987). 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. Sierra-Alvarez and Lattinga (1991) also reported the toxicity due to the presence of a higher concentration of lignin can also have an adverse effect on the biodegradability.

4. MEMBRANE PERFORMANCE

The thermophilic and mesophilic SB-AnMBRs were operated at constant flux of 0.1 $m^3/m^2/d$ throughout the study and variation of transmembrane pressure was observed (Figure 4). According to the membrane manufacturer's recommendation cleaning of membranes is generally required when the TMP exceeds 40 inches of water or if the membranes were ineffective in producing permeate. During the 550 days of operation (mesophilic and thermophilic combined) the TMP was well below 20 inches of water in the mesophilic and thermophilic reactors. On day 193, the membranes in the mesophilic reactor had to be changed as it was observed that there was no collection of the effluent. Membranes were cleaned at this point and flux recovery compared to the flux of virgin membranes was observed with a clean water test. Only 16-20% recovery was observed after cleaning these fouled membranes with 5% citric acid and water (manufacturer's recommendation: 5% citric acid, 0.5% NaOCl, and 2% NaOH). Previous studies reported that carbohydrates are the major components responsible for membrane fouling (Kimura et al., 2005; Rosenberger et al., 2006). But recent reports, also indicates that soluble proteins and carbohydrate should also be considered in the development of membrane fouling in MBRs (Metzger et al., 2007; Tian et al., 2008). Thus, to achieve a higher flux recovery, the membranes were later cleaned with a combined solution of 0.5% sodium hypochlorite (NaOCl) + 2% sodium hydroxide (NaOH). The results are reported in Table 5. NaOCl and NaOH solution cleaning gave an 87% recovery of the flux. NaOCl and NaOH are mostly used to remove the organic foulants and the improved recovery indicates the presence of organics as dominant components of the foulants in this study (Tian et al., 2010).

The membrane performance was considered good with only one fouling event over the operational period for the mesophilic reactor (~300 days). No fouling event in thermophilic reactor (operational period = approx. 250 days) was observed. Continuous biogas scouring, membrane submerged in relatively dispersed sludge and the soluble nature of the wastewater were important reasons for sustaining the flux of 0.1 $m^3/m^2/d$ without detrimental fouling events. This demonstrates that the SB-AnMBR can be operated under both mesophilic and thermophilic conditions without significant membrane fouling at the loading and flux that were applied.

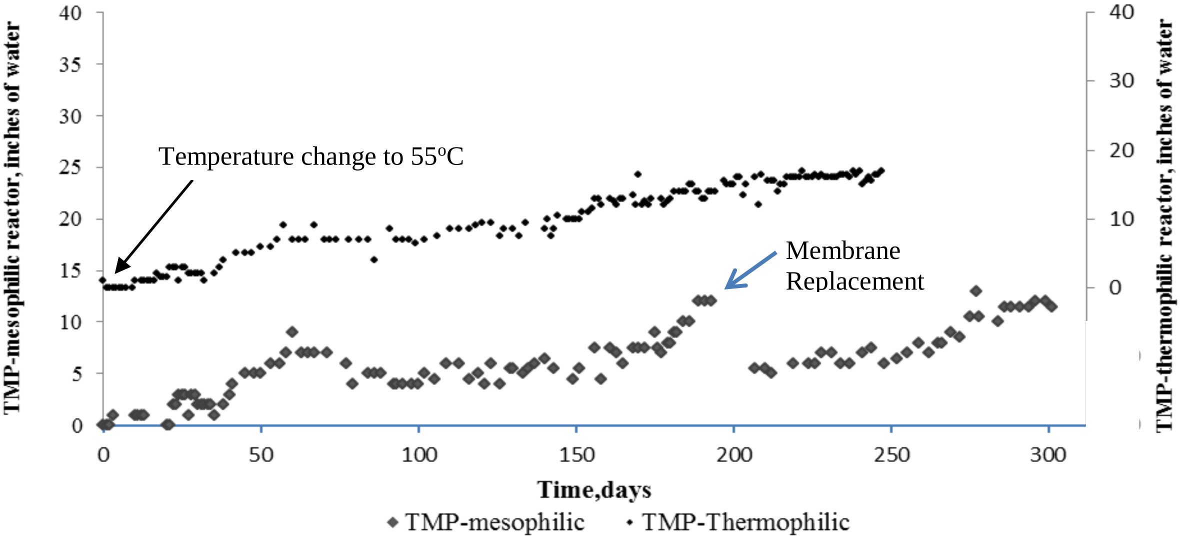

Figure 4. Variation of trans-membrane pressure

Table 5. Flux variation with respect to cleaning methods

Mesophilic Reactor (Day:198): Flux (mL/min)				
Membrane Number	Virgin membrane	Fouled membrane	Cleaning methods	
			5% citric acid	0.5% NaOCl + 2% NaOH
1	985	120	159	853
2	975	135	162	847
3	980	140	166	857

5. CONCLUSIONS

To our knowledge, SB-AnMBR application particularly for PHL from Canadian pulp industry has not been studied previously. 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 $_{\text{(removed)}}$/ d). Acetic acid and furfural were almost completely degraded. Moreover, 60-80 % of lignin was also successfully removed from the waste stream. Overall results indicated that the thermophilic and mesophilic reactor are effective in dealing with high strength waste like PHL. However, further work in terms of economics and technical feasibility of these systems would be needed before firm recommendations could be made to the dissolving pulp industry to replace the current disposal method (evaporation and use of recovery boiler) of PHL.

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