Treatment of kraft evaporator condensate using a thermophilic submerged anaerobic membrane bioreactor

B. Q. Liao, K. Xie, H. J. Lin and Daniel Bertoldo

ABSTRACT

The feasibility of using a thermophilic submerged anaerobic membrane bioreactor (SAnMBR) for kraft evaporator condensate treatment was studied at 55 ± 1°C over 6.5 months. Under tested organic loading rate of 1–7 kg COD/m^3 day, a soluble COD removal efficiency of 85–97% was obtained. The methane production rate was 0.35 ± 0.1 L methane/g COD and the produced biogas was of excellent fuel quality with 80–90% methane. A higher membrane fouling rate was related to the presence of a larger portion of fine colloidal particles (1–10 μm). The thermophilic SAnMBR was sensitive to the presence of toxic compounds in feed and unexpected pH probe failure (leading to a higher pH). Feed toxic shock caused sludge deflocculation and thus deteriorated membrane performance. Operating the reactor as a conventional anaerobic reactor to waste some of the fine flocs in treated effluent during the start-up process was an effective strategy to reduce membrane fouling. The experimental results from this study indicate that treatment of kraft evaporator condensate is feasible in terms of COD removal and biogas production using thermophilic SAnMBRs but pre-treatment may be needed to remove toxic sulfur compounds and membrane fouling caused by the large portion of fine particles may be a challenge.

Key words | kraft evaporator condensate, membrane fouling, submerged anaerobic membrane bioreactor, thermophilic treatment

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INTRODUCTION

Evaporator condensate (EC) from kraft pulping digester and evaporators contains methanol as the main carbon source, and has characteristics of high temperature (50–70°C) and high strength (Blackwell *et al.* 1979). Both aerobic and anaerobic treatments have been used for kraft EC treatment. Conventional activated sludge process, membrane separation bioreactor technology, and anaerobic digestion technology have been tested for kraft EC treatment. Aerobic biological digestion usually provides better quality of treated effluent in terms of effluent color and odor when compared to anaerobic biological treatment alone. However, anaerobic treatment with the incorporation of membrane filtration (e.g. anaerobic membrane bioreactors (AnMBRs)), can provide equal or superior quality of treated effluent as compared to the aerobic treatment, and is more economical than aerobic treatment only (Minami 1994). Furthermore, a reduction in total cost is achieved through energy recovery using the evolved methane gas, reduced production of excess sludge, and less electric power consumption, which is a major energy cost due to aeration in aerobic treatment (Minami 1994).

Compared to mesophilic anaerobic processes, thermophilic anaerobic processes can treat kraft EC at its discharged temperature, consequently saving energy and operational costs on pre-cooling and post-heating process water prior to and after biological treatment. The anaerobic treatment of methanolic wastewater under mesophilic conditions has been investigated by many studies, but so far, very little is known about methanol conversion under thermophilic conditions (Paulo *et al.* 2001). Although there

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are a number of advantages associated with the thermophilic processes, it is generally believed that biomass separation is a challenge under thermophilic temperatures, due to the presence of a larger portion of fine flocs in treated effluent and sludge deflocculation. Therefore, the incorporation of membrane separation technology into the conventional thermophilic anaerobic treatment may overcome biomass separation problems.

Although side-stream AnMBRs were tested for kraft EC treatment (Minami 1994), the side-stream AnMBRs suffer from the high energy cost of recirculating mixed liquor at high velocities to prevent membrane fouling. In addition, floc breakage and loss of biological activity was observed due to pump shear stress (Kim *et al.* 2001). On the other hand, the development of submerged anaerobic membrane bioreactor (SAnMBR) has received much attention in recent years. The use of biogas recirculation for membrane surface scouring can effectively control membrane fouling (Hu & Stuckey 2006; Liao *et al.* 2006; Jeison & van Lier 2008; Lin *et al.* 2009). Nevertheless, at present there is no information available for treating pulp and paper wastewater, such as kraft EC, by using SAnMBRs under thermophilic temperatures. Therefore, the objective of this study was to study the feasibility of using a thermophilic SAnMBR for kraft EC treatment, to quantify COD removal efficiency and biogas production, and to understand and control membrane fouling in the thermophilic SAnMBR.

METHODS

Experimental system

A laboratory-scale SAnMBR system (10 L) was constructed to treat kraft EC. A baffle was used to separate the bioreactor (diameter: 15 cm, height: 50 cm) into two parts: top zone (6.5 L) and bottom zone (3.5 L). A flat sheet microfiltration membrane module, with a membrane area of 0.03 m^2 and a membrane pore size of 0.3 μm, was submerged in the top zone. The bottom zone was used as sludge blanket. A vacuum driven peristaltic pump was employed to acquire permeate from the membrane module. The pump was controlled by a timer, allowing the pump to extract permeate for 4 min, and then shutting the pump off for 1 min. The purpose of the on/off cycle was to slow the membrane fouling process. The permeate flux was controlled by adjusting the pump speed and two calibrations were conducted daily. All membranes used in this study were made of polyvinylidene fluoride (PVDF) materials using phase inversion method. A tubular stainless steel gas sparging diffuser was located underneath the membrane module to provide mixing and to control solids deposition over the membrane surface. This was done by continuously recirculating the headspace biogas through a peristaltic pump at a biogas sparging rate of 0.25–0.75 litre per minute (LPM). A magnetic stirrer was located at the bottom of the bioreactor, where the kraft EC was fed in by another peristaltic pump, to provide necessary mixing of the sludge liquor. The feeding peristaltic pump was controlled by a liquid level sensor controller. The temperature was maintained constant at 55 ± 1°C by recirculating heated water from a temperature-controlled water bath to the water jacket of the reactor. The pH was monitored using a pH electrode (Dulcometer, Fa Prominent), and automatically adjusted to 7.0 using a pH regulation pump and a 0.1 N sodium hydroxide (NaOH) solution.

Feed characteristics

The kraft EC from a local pulp and paper mill had a chemical oxygen demand (COD) of 2,500 ± 100 mg/L. Methanol accounts for 94–96% of the feed COD. A scanning of the metal ions in the feed by inductively coupled plasma-mass spectrometry (ICP-MS) showed that the raw kraft EC did not contain sufficient minerals or nutrients. Therefore, some mineral salts and trace element nutrients were added to the raw kraft EC as suggested in a previous study (Welander *et al.* 1999). The micro-nutrients concentrations are provided below: $MgCl_2$ 0.1 mM, $FeCl_2$ 5 μM, $CaCl_2$ 5 μM, $MnCl_2$ 0.1 μM, $CoCl_2$ 0.1 μM, $NiCl_2$ 0.1 μM, $CuCl_2$ 0.01 μM, $ZnCl_2$ 0.01 μM and $NaSeO_3$ 0.01 μM. Macro-nutrients, nitrogen (NH_4Cl) and phosphorus (KH_2PO_4), were fed in a proportion of COD: N: P of 100: 2.6: 0.4 to sustain the nutrient concentrations required for biomass growth in an anaerobic environment. Additional methanol was added to the feed to test the feasibility of thermophilic SAnMBR for treating higher organic loading rates (ORLs).

Reactor start-up

Mesophilic anaerobic sludge from a full-scale upflow anaerobic sludge blanket (UASB) treating pulping acidic condensate (Tembec, Temiscaming, Quebec) was used as seed to develop thermophilic anaerobic sludge. In the first run, before the addition of a flat-sheet membrane module into the bioreactor, the conventional anaerobic bioreactor was operated as a batch reactor for the first 44 days at 37°C. Effluent was manually discharged from the top taps of the reactor at a rate of 2 litres per day until day 30, then 3 litres per day until day 43. After day 43, a flat sheet membrane was installed to convert the conventional anaerobic reactor into a SAnMBR. After the membrane module was incorporated to the anaerobic bioreactor, the SAnMBR was operated at 37°C for two weeks (day 1–14) to get used to the kraft EC. After that, the SAnMBR temperature was increased from 37°C in stepwise (1–1.5°C/day) to 55°C within 2 weeks (day15–29). The thermophilic SAnMBR was then operated under various ORLs for 60 days. The experiment was terminated at day 95, because of the complete loss of biological activity caused by feed toxic shocking (high concentration of sulfur compounds in feed, like H_2S). In the whole process, no sludge was discharged except for sludge sampling and sludge cake characterization measurements, which corresponded to a sludge retention time of 230 ± 30 days. The operation was stopped and a physical cleaning procedure was carried out when the transmembrane pressure (TMP) reached 30 kPa, and resumed after washing of fouled membranes. This occurred because it was difficult to maintain the flux at a constant level at a TMP of over 30 kPa.

A second run was started on day 96. 10 days was allowed to develop the thermophilic sludge from mesophilic sludge seed (37°C) by increasing the reactor temperature 1–2°C/day in stepwise. The membrane module was installed from day 1 of the second run. The second run of the thermophilic SAnMBR was operated for 105 days.

The membrane flux was maintained at 5.4 ± 0.9 and 2.2 ± 0.6 L/m^2 h, respectively, during the first and second run. Initially, the thermophilic SAnMBR in the second run was operated at the same flux as that in the first run. However, the membrane flux in the second run could not be maintained at the desired level used in the first run due to serious membrane fouling. Therefore, a lower membrane flux was maintained in the second run to sustain its operation. The mixed liquor suspended solids (MLSS) concentration in the top zone was 5 ± 1 and 6 ± 2.5 g/L, respectively, in the first and second run.

The purpose of the two different start-up procedures used in the first and second run was to study the impact of start-up procedures on the performance of thermophilic SAnMBR. Previous studies on thermophilic SAnMBRs found the accumulation of fine flocs resulted in a deterioration of the membrane performance (Jeison & van Lier 2008).

Analytical methods

All mixed liquor samples collected for supernatant COD analysis were first centrifuged at 18,700 × g. The supernatant was then filtered through a 0.45 μm pore size filter paper to remove fine suspended material and any residual biomass before being analyzed for supernatant chemical oxygen demand (COD). COD and MLSS were measured according to Standard Methods (APHA 2005). Particle size measurements were made using a Malvern Instruments particle size analyzer (Malvern mastersizer 2000, UK). Biogas samples were taken from the headspace of the reactor, while the composition of the biogas (methane, nitrogen and carbon dioxide) was determined and quantified using a Shimadzu (Kyoto, GC-201) GC-TCD fitted with a silica gel packed column (5,486 × 3.18 mm). The amount of biogas produced was determined by a liquid displacement arrangement.

Calculation of the total membrane resistance

According to Darcy law, filtration resistances are calculated using the following equation:

$$R_t = R_m + R_c + R_p = \frac{\Delta p_T}{\eta \times J} \quad (1)$$

where, R_t is the total hydraulic resistance (1/m), R_m is the membrane resistance (1/m), R_p is the pore blocking resistance (1/m), R_c is the cake layer resistance (1/m), Δp_T is the transmembrane pressure (Pa), η is the dynamic viscosity (Pa s) and J is the membrane flux (m^3/m^2 s).

Each resistance value was determined using the same membrane module used in the pilot-scale SAnMBR submerged in a mini-MBR with effective volume of 2.5 L. The experimental procedure to determine each resistance value was as follows: (1) R_m was estimated by measuring the water flux of tap water; (2) R_t was evaluated by the final flux of biomass microfiltration; (3) the membrane surface was then flushed with tap water and cleaned with a sponge to remove the cake layer. After that, the tap water flux was measured again to obtain the resistance of $R_m + R_p$. From steps (1)–(3), R_t, R_m, R_p and R_c could be calculated.

Membrane fouling rate (ΔR) of the mixed liquor was calculated as ΔR_{24} (1/(m h)), the change rate of R within the initial 24 h of filtration, according to Equation (2):

$$\Delta R_{24} = \frac{R_{24} - R_0}{\Delta t} \quad (2)$$

where Δt is filtration time (h), R_0 and R_{24} are the total resistance of the membrane at starting time and after 24 h filtration, respectively (1/m).

RESULTS AND DISCUSSION

Soluble COD removal and biogas production under various influent COD loadings

Figure 1 shows the thermophilic SAnMBR soluble COD concentrations in the feed, supernatant, and permeate over time. The permeate COD was in the range of 50–200 mg/L under normal operation, which corresponded to a COD removal efficiency of 80–95%. The COD removal efficiency

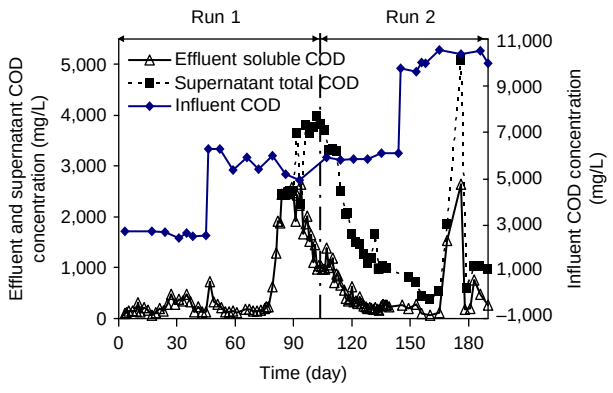

Figure 1 | Influent, supernatant and permeate COD.

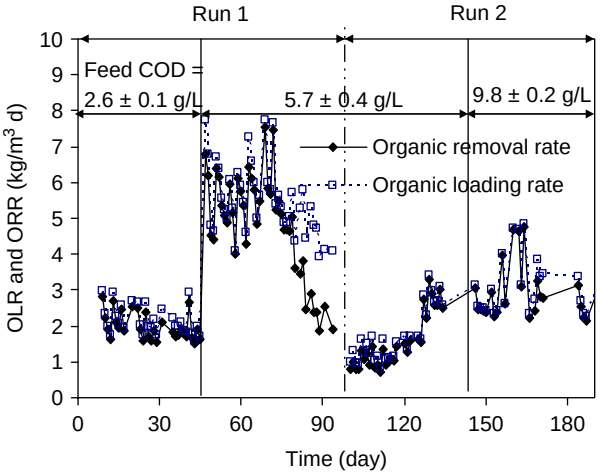

Figure 2 | OLR and ORR vs. time.

deteriorated slightly from 95% to 85% during the transition from mesophilic (37°C) to thermophilic temperature (55°C) (day 15–29). But after this time, the COD removal efficiency recovered back to 95% within one week. This removal efficiency was maintained until day 70, when a feed toxic shocking occurred. The feed toxic shocking resulted in a significant loss of biological activity, with no biogas production and significant low COD removal efficiency. The thermophilic SAnMBR showed no sign to recover within 3 weeks and thus this run was terminated at day 95. Therefore, the thermophilic SAnMBR was re-inoculated with 3.5 L seed sludge on day 96. After acclimation and stabilization, the overall average permeate COD concentration was 187 mg/L and a 96.8% COD removal was attained under normal operation. An elevated pH disruption during day 165 resulted in a loss of biological activity and reduced COD removal. It took about two weeks for the thermophilic SAnMBR to recover its biological activity. Figure 2 shows the change in organic loading rate (OLR) and organic removal rate (ORR) with experimental time. The tested OLR range was from 1 to 7 kg COD/m^3/day. The ORR was close to ORL, implying a high COD removal efficiency. However, the OLR in the second run was much lower than that used in the first run, due to the limited membrane flux caused by membrane fouling as discussed later.

It is interesting to note that there are significant differences between the supernatant COD in the bioreactor and the permeate COD (Figure 1). This is consistent with

the findings of previous studies (Huang *et al.* 2000; Hu & Stuckey 2006) indicating the sieving effect of the membrane and sludge cake on membrane surfaces. The significantly higher supernatant COD and the lower COD removal efficiency from day 100 to day 130 was probably caused by sludge digestion at a lower OLR (1 kg/m^3/day), as indicated by a decrease in mixed liquor concentration. An increase in the supernatant COD was also observed during the period of pH disruption (day 165–178). This is consistent with the findings of Aquino & Stuckey (2004) in that more SMPs could be produced during unstable conditions.

Biogas composition and production

Figures 3 and 4 show the variation of biogas component (N_2, CH_4, and CO_2) concentration and methane yield with experimental time from the thermophilic SAnMBR, respectively. Under normal operation, the biogas contained about 80–90% methane, 6–10% carbon dioxide and 3–5% nitrogen. A relatively high nitrogen concentration (10–16%) was observed in biogas at the beginning of the first run. This could be due to the residual nitrogen after membrane cleaning. Nitrogen was used to sparge the bioreactor to remove oxygen when the membrane module was cleaned and re-installed in the bioreactor. The volume of biogas produced was not enough to replace the nitrogen gas at a high frequency of membrane cleaning.

The average methane production rate in the thermophilic SAnMBR, during an OLR of 2–7 kg COD/m^3/day, from day 38 to day 75, was 0.3 L CH_4/g COD. The decrease in methane yield from day 70 to 90 was caused by toxic

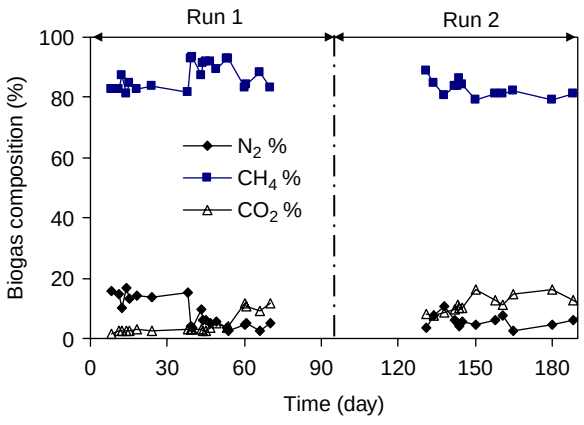

Figure 3 | Biogas composition and concentration.

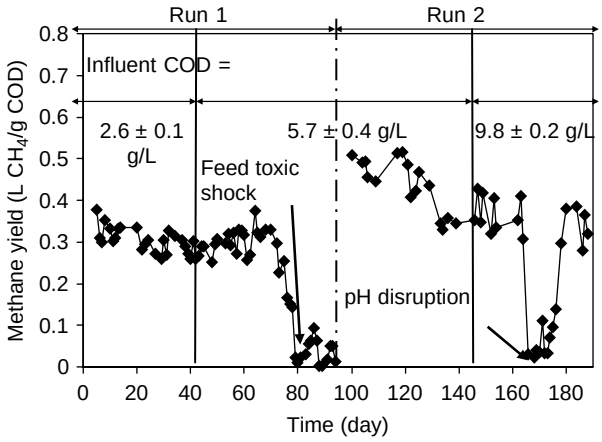

Figure 4 | Methane yield with time.

influent, and the thermophilic SAnMBR system was not able to recover from it, even when the toxic influent was replaced by a non-toxic feed. This demonstrated the poor ability of the thermophilic SAnMBR to handle unexpected system upsets and feed toxic shocks. At the beginning of the second run, a relatively higher methane yield (0.4–0.5 L CH_4/g COD) was observed (day 100–128). This might be caused by the additional contribution of sludge digestion under the lower OLR (1.5 ± 0.5 kg COD/m^3/day). When the OLR was increased to 4 ± 1 kg COD/m^3/day after day 130, the methane yield was reduced to 0.35 ± 0.1 L CH_4/g COD. This is more consistent with the results obtained in the first run. Although the results from previous studies suggest a higher methane yield under the thermophilic conditions, the results from this study suggest that methane yield is comparable to or higher than that of mesophilic treatment (Dufresne *et al.* 2001). The higher methane yield could be attributed to a larger contribution of the higher sludge digestion rate under thermophilic temperatures.

Sludge properties and membrane fouling

Figures 5 and 6 show the comparison of particle size distribution of the top zone mixed liquor between the first run and the second run and before and after feed toxic shocking, respectively. The results (Figure 5) show one single peak of the particle size distribution of top zone mixed liquor, ranging from 2 to 50 μm with a mean size of 9.5–10 μm in the first run and two distinct peaks, one in the

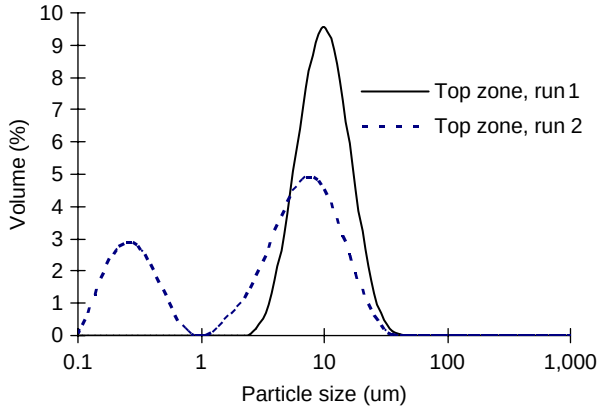

Figure 5 | Particle size distribution between Run 1 and Run 2.

range of 0.1 to 1 μm with a mean size of 0.25–0.27 μm, and the other in the range of 1 to 50 μm with a mean size of 7–8 μm in the second run. The results suggest that the start-up process had a significant impact on the accumulation of fine flocs in the thermophilic SAnMBR. The operation of the thermophilic bioreactor as a conventional batch reactor in the first run wasted most of the fine flocs in treated effluent and thus had no floc size less than 1 μm in the top zone when the membrane module was installed. While all the large and fine flocs were retained in the thermophilic SAnMBR in the second run as membrane module was in place from the first day of operation. The accumulation of fine flocs in the thermophilic SAnMBR explained the significant difference in membrane filtration resistance (Table 1) between the first and the second run. The total membrane filtration resistance in the second run was 3–5 times of that in the first run. This could be attributed to smaller flocs having a strong tendency to deposit on membrane surfaces and thus forming sludge cake layers due to their low back transport velocities (Belfort *et al.* 1994). From Table 1, it is clear that sludge cake formation was the dominant mechanism of membrane fouling and pore clogging was not significant in both runs. The results are consistent with the findings of Jeison & van Lier (2008) in that the accumulation of fine flocs deteriorated the membrane performance in thermophilic SAnMBRs.

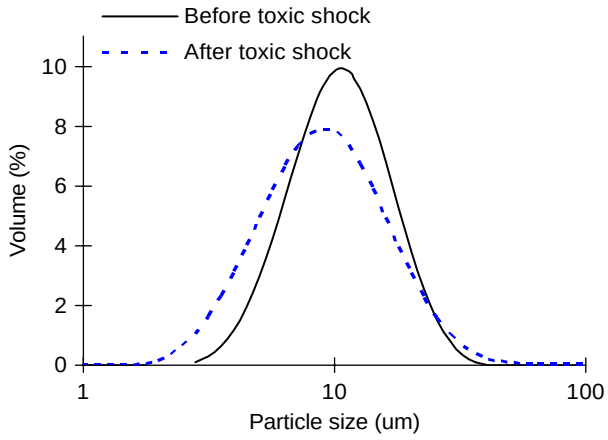

Figure 6 | Particle size distribution before and after feed toxic shocking.

Table 1 | Comparison of resistances between the first and second run

	R_m ($\times 10^{12}$ m^{-1})	R_p ($\times 10^{12}$ m^{-1})	R_c ($\times 10^{13}$ m^{-1})	R_t ($\times 10^{13}$ m^{-1})
Run 1	0.57 (2.8%)*	0.71 (3.4%)*	1.93 (93.8%)*	2.06 (100)*
Run 2	0.57 (0.8%)*	0.77 (1.0%)*	7.31 (98.2%)*	7.44 (100)*

*Percentage of the total resistance R_t shown in parentheses.

Membrane fouling rates (ΔR) before and after the feeding toxic shock were 7.8 ± 1.6 and 14.9 ± 0.8 × 10^{11} m^{-1} h^{-1}, respectively. The significant higher membrane fouling rate after feed toxic shocking could be explained by the change in floc size distribution (Figure 6). Feed toxic shocking caused sludge deflocculation. An increase in the fraction of fine flocs resulted in an increase in membrane filtration resistance. It took about two weeks after feed toxic shocking for the thermophilic SAnMBR to recover the membrane performance.

CONCLUSIONS

The feasibility of using a thermophilic SAnMBR for kraft EC treatment was studied. The main conclusions are summarized below:

(1) The results show that kraft EC treatment using an SAnMBR is feasible under thermophilic conditions in terms of COD removal and biogas production. Under tested OLR of 1–7 kg COD/m^3/day, a COD removal efficiency of 85–97% was achieved. The methane yield was 0.35 ± 0.1 L CH_4/g COD removal with an excellent fuel quality close to 85–90% methane in the biogas.

(2) Membrane fouling may be a challenge for the operation of the thermophilic SAnMBR. A higher

membrane fouling rate was observed when a larger portion of fine colloidal particles were present in the mixed liquor. Operation of the bioreactor as a conventional anaerobic bioreactor during the start-up process was an effective strategy to waste the fine colloidal particles in the effluent before the installation of membrane modules to minimize the impact of fine colloidal particle on membrane fouling.

(3) The thermophilic SAnMBR was sensitive to the toxic compounds in the feed and elevated pH disruption. Feed toxic shock and pH shock caused deterioration of biological activity and biogas production. Pre-treatment of the feed may be required to remove toxic sulfur compounds to sustain thermophilic biological activity.

(4) Feed toxic shock caused sludge deflocculation and thus deteriorated membrane performance by increasing membrane fouling rate.

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