Comparison of thermophilic and mesophilic anaerobic treatments for potato processing wastewater using a contact reactor

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Abstract

In this study, different organic loading rates (OLRs) ranging from 1.1 to 5.0 kg COD/m³·day were used to assess the performance of an anaerobic reactor at the optimum mesophilic (35°C) and thermophilic (55°C) temperatures. The methane gas production rate of the thermophilic treatment was higher than that of the mesophilic treatment. The efficiency of chemical oxygen demand (COD) removal was observed to range from 89.12 to 93.20% following the thermophilic anaerobic treatment and from 76.36 to 92.62% following the mesophilic treatment. The average VFA (volatile fatty acid)/alkalinity ratio of the effluent was 0.3 under both thermophilic and mesophilic conditions for all the OLR applications. The HPr/HAc (propionic acid/acetic acid) ratio was calculated as 0.16 and 1.3 for the mesophilic and thermophilic treatments, respectively. For the mesophilic treatment, the average methane gas production was found to be 0.394 m³ CH₄/kg COD_removed while it was 0.42 m³ CH₄/kg COD_removed for the thermophilic experiment. However, the sludge settleability of the mesophilic treatment was better than that of the thermophilic treatment.

Keywords: mesophilic, thermophilic, anaerobic treatment, wastewater, contact reactor

1. Introduction

Anaerobic wastewater treatment differs from conventional aerobic treatment in that in the former, no aeration is applied. The lack of oxygen leads to controlled anaerobic conversions of organic pollutants to carbon dioxide and methane, the latter of which can be utilised as an energy source. The main advantages of anaerobic treatment include operability at very high loading rates (10 to 20 times as high as in the conventional activated sludge treatment) and less operating costs and reduced waste sludge.

Anaerobic treatment can be conducted at psychrophilic (<25°C), mesophilic (25-40°C), and thermophilic (>45°C) temperatures (El-Mashad *et al.* 2004). However, only mesophilic and thermophilic ranges provide optimum anaerobic conditions for the production of methane. The mesophilic range is between 20°C and 40°C with the

optimum temperature being 35°C. The thermophilic temperature ranges from 50°C to 65°C with an optimum temperature of 55°C.

The effect of temperature changes on the first stage of the digestion process (hydrolysis and acidogenesis) is not very significant. The second and third stages of decomposition can only be performed by certain specialised microorganisms (acetogenic and methanogenic bacteria) and thus, these are much more sensitive towards changes in temperature. However, an important characteristic of anaerobic bacteria is the decrease of the decomposition rate below 15°C. Thus, it is possible to maintain the activity of anaerobic sludge for longer periods. This is especially useful in the anaerobic treatment of wastewater in seasonal industries such as sugar mills.

As in all biochemical reactions, the anaerobic degradation rate of organics increases with temperature. However, the effect of temperature is often less than predicted by the van't Hoff equation, which establishes that chemical reaction rates double with each 10°C rise in temperature (Switzenbaum & Jewell, 1980). There are also certain disadvantages of temperature changes on anaerobic treatment, such as resulting in poor sludge settling that brings about high-effluent suspended solids, effluent turbidity and biomass washout (Ahn & Forster, 2002).

Food processing wastewaters, such as wastes from coffee processing, palm oil mill, cannery, distillery and ice-cream are often discharged at or above ambient temperatures. Treating these effluents under conventional mesophilic conditions requires costly pre-cooling, and also has the risk of losing biomass activity in case of a breakdown of the cooling system (Yu *et al.* 2002). Therefore, thermophilic treatment is an attractive alternative for these wastewaters (Ahn & Foster, 2000). Furthermore, in the thermophilic range, biodegradation occurs faster compared to mesophilic conditions; thus, the organic loading potentials of thermophilic anaerobic reactors are substantially higher (Ahn & Foster, 2002). Despite having several significant advantages, thermophilic anaerobic treatment has certain drawbacks; e.g., it is mostly favourable for the production of propionate, for which

further degradation is slower than in other VFAs and this type of treatment is more sensitive to environmental changes (McInerney, 1988; Yu *et al.* 2002).

Earlier studies investigating the effect of temperature on the anaerobic treatment process have mainly focused on the comparison of steady-state performance at two or more fixed operating temperatures (Kim *et al.* 2002; Ndegwa *et al.* 2008; Yilmaz *et al.* 2008). The effect of temperature fluctuations on anaerobic treatment efficiency has been also studied. It has been reported that a temporary decrease in temperature (between 10 and 20°C) only temporarily affects the performance and stability of psychrophilic anaerobic reactors treating swine manure (Massé *et al.* 2003). However some of the studies conducted within the thermophilic range indicated that thermophilic process is more susceptible to environmental and operational conditions such as temperature than mesophilic process (Ahring *et al.* 2001; Iranpour *et al.* 2005). El-Mashad *et al.* (2004) found that the imposed daily upward temperature fluctuation affected the maximum specific methanogenic activity more severely than the daily downward temperature fluctuations in completely stirred tank reactors (CSTRs).

Despite the availability of comparisons between mesophilic and thermophilic anaerobic wastewater treatments in the literature, none of the published studies has reported experiments with an anaerobic contact reactor. Therefore, in the present study, we chose to investigate the performance of an anaerobic contact reactor under mesophilic (35°C) and thermophilic (55°C) conditions. This paper presents the comparison of the efficiency of the mesophilic- and thermophilic-treated anaerobic contact reactor in terms of COD removal, composition of biogas and VFAs.

2. Material and Method

2.1. Wastewater Characterisation

The wastewater used in this study was obtained from a factory producing potato chips, maize chips and other snacks.

Table 1. Wastewater characteristics (after peeling and cutting processes)

Parameter	Unit	Range
TCOD	g/L	5.25 - 5.75
SCOD	g/L	2.50 - 3.00
BOD_5	g/L	4.00 - 5.0
Alkalinity	g $CaCO_3$/L	2.00 - 2.50
pH	-	7 – 8
Temperature	°C	15 - 20
TKN	g /L	0.20 - 0.25
NH_3-N	g /L	0.05 - 0.06
Sulphate	g/L	0.40 - 0.50
Total Solid	g/L	4.80 - 5.00
Total Suspended Solids	g/L	2.00 - 2.10
Total Volatile Solid	g/L	4.40 - 4.50

TCOD: Total Chemical Oxygen Demand; SCOD: Soluble Chemical Oxygen Demand; BOD_5: 5-day Biochemical Oxygen demand; TKN: Total Kjeldahl Nitrogen; NH_3-N: Ammonia-Nitrogen

The wastewater produced during peeling and cutting processes was obtained as a grab sample at a volume of 100 L and was kept at 4°C for a week. After each week, a new sample of 100 L was collected due to the fast degradation of wastewater. This process was repeated throughout the study period. Since wastewater has a COD/N/P ratio of approximately 275/10/1 (see all characteristics in Table 1), there was no need for a supplement to adjust the nutrient level for an anaerobic treatment.

2.2. Anaerobic Contact Reactor

Figure 1 presents the anaerobic contact reactor used in this study. Detailed information about the configuration of this reactor is given in our previous study (Şentürk *et al.* 2010). The reactor was inoculated with anaerobic granular sludge obtained from an anaerobic treatment plant in a potato-processing factory. A 10 L heater tank was attached to the system to maintain the reactor temperature at 35±2°C and 55±2°C for mesophilic and thermophilic experiments, respectively. The pH of the system was monitored and controlled continuously using a pH meter. The water used for gas washing was acidified to pH 3 by the addition of HCl and NaCl in order to prevent biogas dissolution. The system was equipped with a heat-insulated separation tank to prevent microorganism loss. A programmable logic controller (PLC/Siemens S7 300) was utilised to ensure that the system was working effectively. Data were obtained and visualised using WinCC SCADA (Siemens).
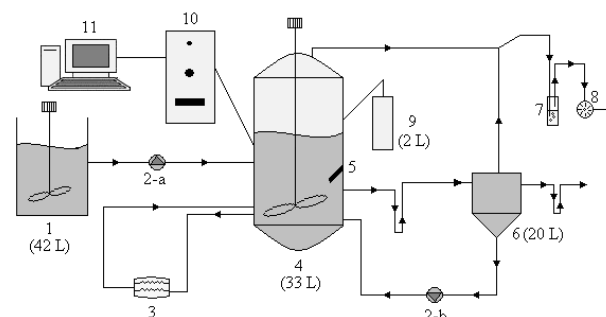
Figure 1. The schematic view and flow chart of the system used in this study; 1) Feed tank, 2 a-b) Peristaltic Pump, 3) Heater, 4) Anaerobic Contact Reactor, 5) pH meter, 6) Separation Tank, 7) Gas washing, 8) Gas meter, 9) NaOH tank, 10) PLC Panel, 11) Computer

2.3. Analytical Methods

All the chemicals were of analytical reagent grade and distilled water was used during all experiments. The COD and BOD_5 analyses were performed according to the STM 5220 C and STM 5210 B methods, respectively (APHA, 2005) and the TKN and NH_3 concentrations were determined with the STM 4500-Norg B Macro-Kjeldahl and STM 4500-NH_3 C methods, respectively (APHA, 2005). The STM 4500-SO_4^{2-} method was utilised for sulphate analyses. The alkalinity and total volatile fatty acid concentrations were measured by the STM 2320 B and

STM 5560 C methods, respectively (APHA, 2005). In addition, each volatile fatty acid concentration was further analysed by a gas chromatograph (Agilent) equipped with an FID detector and a Zebran ZB-Wax capillary column, 30 m × 250 μm × 0.50 μm. Helium was used as the carrier gas. The temperature of the oven was initially set at 100°C for 1 min and then, it was gradually increased to 120°C by 20°C/min followed by an increase of 6.13°C/min up to 205°C. The total duration of this process was 15.87 minutes. The temperature of the detector was 240°C. The samples taken from the reactor were centrifuged at 10000 rpm for 15 minutes at room temperature before being analysed by gas chromatography (GC). The total solids and total volatile solids concentrations were determined (STM 2540 B and STM 2540 C methods, respectively) (APHA, 2005).

The biogas generated was cumulatively measured using a wet gas meter (Ritter, Drum type, TG 05 Model, flow rate of 1-60 L/h). The content of the biogas (CH_4, CO_2, H_2) was analysed by GC (Agilent) using an HP Plot Q + Molecular Sieve column, 60m × 530μm × 400μm. Argon was used as the carrier gas with a gas flow of 4 mL/min. The oven temperature was initially set at 50°C for 5 min followed by a gradual increase of 5°C/min up to 80°C, at which it was maintained for 3 minutes. Then, the temperature was increased by 10°C/min to 100°C. This process took 16 minutes. The temperature of TCD was 200°C. Significant differences were determined between the two temperatures (mesophilic and thermophilic) and different OLRs using a two-factor ANOVA.

2.4. Experimental design

To investigate the effect of temperature on the anaerobic contact reactor, the reactor was operated at two different temperatures, 35°C and 55°C. At both temperatures, the performance of the reactor was assessed at different organic loading rates (OLRs) ranging from 1.1 to 5.0 kg COD/m³. The hydraulic retention time (HRT) values at the corresponding OLRs were calculated from the quotient of the effective reactor volume to wastewater flow rate (Table 2). During the study, each parameter (COD, intermediate of VFAs, composition of biogas) were analysed at steady-state for each OLR.

Table 2. HRT values at corresponding OLRs

| OLRs (kg COD/m³·day)	HRT (day)
1.1	5.11
1.5	3.71
2.5	2.13
3.35	1.64
4.5	1.15
5	1.06

3.   Results and discussion

3.1. COD removal efficiency

It is known that anaerobic reactors demonstrate better process stability under mesophilic conditions compared to thermophilic conditions (Yu *et al.* 2002; Poh and Chong, 2009). However, in this study, the system quickly adapted to the increase in OLRs at both temperatures (35±2°C and

55±2°C) without demonstrating any reduced efficiency. This can be mainly attributed to a CSTR being used (Meynel, 1976; Şentürk *et al.* 2010) and wastewater being composed of easily biodegradable pollutants such as carbohydrates and proteins (Hadjivassillis *et al.* 1997; Şentürk *et al.* 2010). The efficiency of the reactor in terms of COD removal ranged from 89.12 to 93.20% following thermophilic treatment and from 76.36 to 92.62% under mesophilic conditions (Figure 2).

The COD removal efficiency was decreased with the increased OLRs due to the decrease in HRT. As shown in Figure 2, the COD removal efficiency of the reactor was lower under mesophilic conditions since the biodegradation rate was insufficient for the corresponding HRT. These results are consistent with those reported by several researchers including Borja *et al.* (1995), Ahn and Forster (2000), Ahn and Forster (2002) and Yilmaz *et al.* (2008). At lower loading rates, there was only a slight difference between the two temperatures in term of the removal efficiency; however, this difference became greater with the increasing OLRs. When OLRs were increased to 8 kg COD/m³·day under thermophilic conditions, the COD removal efficiency was calculated to be approximately 84%. This indicates that thermophilic anaerobic treatment can be used for higher OLRs, which supports the results reported by Ahn and Forster (2000).
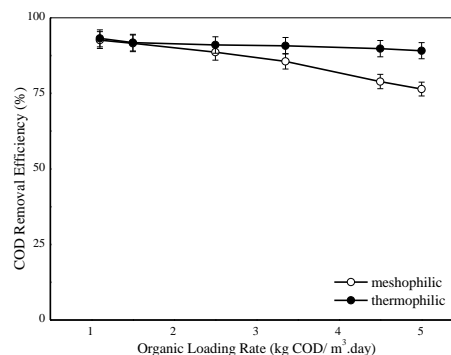

Figure 2. COD removal efficiency of the anaerobic reactor at mesophilic and
thermophilic temperatures and different OLRs.

3.2. Intermediate products, pH and alkalinity

At the beginning of an anaerobic treatment, as a result of the hydrolysis and acidification process, VFAs are produced by microorganisms (Valentini *et al.,* 1997). At this stage, VFA production rate mainly depends on the characteristics of wastewater, environmental conditions such as temperature and pH, reactor type and operating parameters such as HRT (Jayaseelan & Matsuo, 1995).

As shown in Figure 3, although an increase in the VFA was observed at the initial days of organic loading, pH was not observed to change at mesophilic and thermophilic temperatures. The main reason for this was the high alkalinity of the potato-processing wastewater creating a buffer effect. In this study, the maximum VFA/alkalinity

ratios for thermophilic and mesophilic conditions were found to be 0.3 and 0.5, respectively. Both values being well below the limit value of 0.8 resulted in an inhibitory effect (Water Pollution Control Federation, 1987). Therefore, there was no need to add any chemicals such as NaOH and NaHCO₃ to the system to adjust the pH. In addition, alkalinity was formed in the reactor by the reaction of ammonia with carbon dioxide and water to form ammonium bicarbonate (Zhao & Viraraghavan, 2004; Şentürk *et al.*, 2010). One of the major criticisms about the use of thermophilic digestion is that the final effluents contain higher concentrations of VFAs compared to mesophilic digesters (Hill *et al.*, 1985).
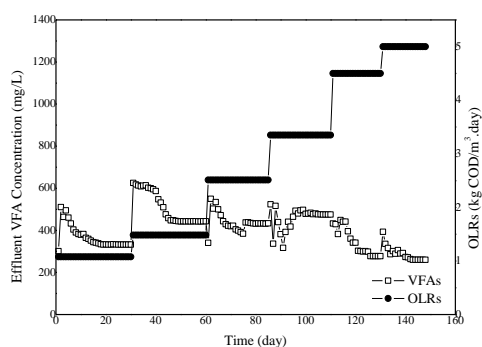
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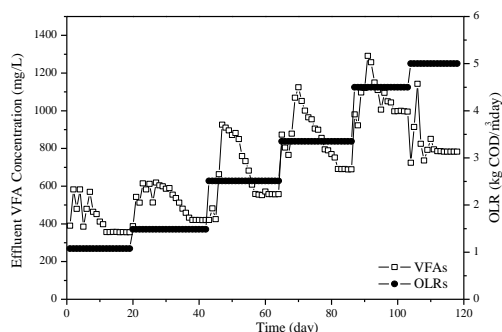
(b)

Figure 3. Effluent VFA concentrations at different OLRs (a) thermophilic, (b) mesophilic

Similarly, Harris and Dague (1993) reported that thermophilic filters produced an effluent with VFA concentrations greater than in the effluent from a mesophilic filter. Contrary to these reports, in the present study, the effluent VFA concentration of the mesophilic treatment was found to be higher than that of the thermophilic treatment, which resulted in a higher biodegradation rate under the latter conditions.

Determination of the composition of VFAs is great sinificant in anaerobic wastewater treatment, since it gives information about the metabolic pathway of the process. HAc is the most important intermediate in the production of methane. Transformation of HAc and n-HBu to methane is faster than conversation of HPr, n-HVa, and i-HVa to methane. When the system reached to steady-state at each OLR, the concentrations of VFA species are given Table 3. The degradation of straight chain (normal form) VFAs is faster than their branched (iso formed) forms. In thermophilic condition, the biological degradation of HPr increased linearly with the increasing OLR up to 2.5 kg COD/m³·day, after this loading, it decreased owing to inadequate HRT. HAc having 2 carbons is directly converted to CH_4 and CO_2 by methane bacteria. But, the VFAs having more carbons than 4 cannot be converted directly by methane archaea. That's why, VFAs with high moleculer weight are transformed to HAc prior to CH_4. Regarding the concentration of VFA species under mesophilic condition, HAc was higher than the others, making it the final VFA product prior to the production of methane (Ahn & Forster, 2000; Yilmaz *et al.* 2008). In contrast, under thermophilic condition, HAc lesser than the other VFA species, probably due to accelerate in performance of methane archaea according to Arhenius equation. The HPr/HAc ratio was calculated to be 0.06 - 0.25 and 1.13 - 1.25 for mesophilic and thermophilic treatments, respectively. As known, if this ratio reaches 1.4, the system would fail (Buyukkamaci & Filibeli, 2004).

3.3. Gas production and composition

The results clearly indicate that the process was efficient in terms of biogas production and yield at all loading rates for both mesophilic and thermophilic conditions. Figure 4 presents the daily produced biogas volumes. Although biogas production increased with the increasing loading rates (Dinsdale *et al.* 1997; Ahn and Forster, 2000), methane had an inverse proportion to OLRs due to low HRT (Yu *et al.* 2002) with the methane percentages ranging from 80-89 and 79-89 for mesophilic and thermophilic temperatures, respectively.
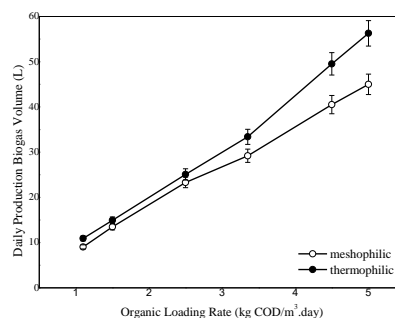
Figure 4. Daily biogas production under mesophilic and thermophilic conditions at different OLRs.

As illustrated in Figure 4, there was a linear correlation between biogas production and OLRs. It should be noted that with the increase in OLRs, the methane content of biogas slightly decreased in consistency with the available theoretical information (Metcalf & Eddy, 2003). The average methane production was found to be 0.394 m³

CH_4/kg $COD_{removed}$ following the mesophilic treatment and 0.42 m^3 CH_4/kg $COD_{removed}$ following the thermophilic treatment. These results show that in terms of methane production, thermophilic anaerobic treatment was better than mesophilic anaerobic treatment (Borja *et al.* 1995; Ahn & Forster, 2000; Ahn & Forster, 2002; Yu *et al.* 2008; Yilmaz *et al.* 2008).

Table 3. VFAs composition at different OLRs for thermophilic and mesophilic.

Organic Loading Rate (kg COD/m³·day)	Thermophilic (55°C)								Mesophilic (35°C)							
	HAc	HPr	n-HBu	i-HBu	n-HVa	i-HVa	n-HCa	i-HCa	HAc	HPr	n-HBu	i-HBu	n-HVa	i-HVa	n-HCa	i-HCa
1.1	27.38	31.02	10.00	41.73	27.38	0.00	52.23	54.35	185.45	20.42	34.57	34.50	20.42	10.46	14.48	20.23
1.5	31.25	39.40	39.90	59.10	31.25	48.8	50.5	52.50	284.05	17.04	15.05	14.20	21.54	12.45	17.89	10.02
2.5	40.61	49.88	55.01	55.88	40.61	55.13	51.17	55.67	313.07	26.92	17.94	13.96	24.61	23.98	48.59	29.29
3.35	33.42	41.74	41.15	55.89	33.42	50.03	53.92	57.29	361.79	67.34	49.80	47.80	49.92	49.02	53.44	30.53
4.5	24.26	30.38	33.21	38.39	24.26	36.75	32.37	33.46	398.25	96.94	89.16	87.60	78.45	77.62	89.44	46.35
5	17.47	20.64	39.84	38.22	21.47	31.75	30.47	26.25	328.52	69.90	59.28	55.68	54.13	50.47	77.83	21.13

HAc: Asetic acid; HPr: Propiyonic acid; HBu: Butiric acid; HVa: Valeric acid; HCa: Caproic acid; i-: iso; n-: normal

Table 4 presents the content of the produced biogas. Hydrogen was only determined following the thermophilic treatment at the first OLR. At all other OLRs, fermentative hydrogen-producing bacteria may have been washed out from the reactor due to the decrease in HRT with the increasing OLR (Guo *et al.* 2008). It has previously been reported that hydrogen is produced via ß-oxidation during the conversion of long-chain fatty acids (Abdel-Halim, 2005).

Table 4. Content of biogas at different OLRs at mesophilic and thermophilic temperatures

OLR (kg COD/m^3.day)	Mesophilic (35°C)		Thermophilic (55°C)	
	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)
1.1*	11.14	88.86	10.72	88.56
1.5	11.23	88.77	12.00	88.00
2.5	13.95	86.05	11.88	88.12
3.35	14.36	85.64	12.42	87.58
4.5	18.55	81.45	16.22	83.78
5	20.03	79.97	21.00	79.00

*0.72 % H_2 was detected

Therefore, in the present study, it was considered that hydrogen-consuming microorganisms, such as methanogens, reduced the hydrogen gas due to this conversion. The deterioration of hydrogen gas production with the increasing substrate concentration was in agreement with other reports (Oh *et al.* 2004; Van Ginkel & Logan, 2005; Zhang *et al.* 2007; Şentürk *et al.* 2010). We

thus attributed the reduced production of hydrogen gas to the slower β-oxidation process at the mesophilic temperature compared to the thermophilic temperature.

The results of this study also showed that the carbon dioxide percentage in the biogas increased with the increasing OLR probably due to the insufficient HRT corresponding to the OLR values under both conditions (Poh & Chong, 2009). The high carbon dioxide percentages could be a result of the improper balance between the substrate supply, temperature and/or digestion time (Zhao & Viraraghavan, 2004). In addition, under thermophilic conditions, due to low solubility in water, the concentration of carbon dioxide in the biogas increases (Abdel-Halim, 2005). As the percentage of carbon dioxide in biogas increased, methane production decreased. Therefore, it was concluded that HRT did not directly affect the gas composition. Other researchers have also reported that the produced biogas composition mainly depends on the nature of substrates (Zhao & Viraraghavan, 2004).

According to the results of the ANOVA analysis, there was a significant difference in the percent of CO_2 and CH_4 contained in biogas produced at different OLRs ($p < 0.05$). However, there was no significant difference between the mesophilic and thermophilic treatments ($p > 0.05$) in terms of the composition of the produced biogas (Table 5). The increase in temperature led to an increase in the amount of biogas but did not have any effect on the biogas composition.

Table 5. The results of the two-way ANOVA analysis

		CO_2			CH_4		
Summary	**Count**	**Total**	**Mean**	**Variance**	**Total**	**Mean**	**Variance**
Mesophilic	6	89.26	14.87667	13.68735	510.74	85.12333	13.68735
Thermophilic	6	84.24	14.04	15.1336	515.04	85.84	14.26384
OLR (1.1)	2	21.86	10.93	0.0882	177.42	88.71	0.045
OLR (1.5)	2	23.23	11.615	0.29645	176.77	88.385	0.29645
OLR (2.5)	2	25.83	12.915	2.14245	174.17	87.085	2.14245
OLR (3.35)	2	26.78	13.39	1.8818	173.22	86.61	1.8818
OLR (4.5)	2	34.77	17.385	2.71445	165.23	82.615	2.71445
OLR6 (5)	2	41.03	20.515	0.47045	158.97	79.485	0.47045

Source of variation		SS	df	MS	F	P-value	F crit
CO_2	Temperature	2.100033	1	2.100033	1.911287	0.225384	6.607891
	OLRs	138.611	5	27.72219	25.23059	0.001479	5.050329
	Fault	5.493767	5	1.098753			
	Total	146.2048	11				
CH_4	Temperature	1.540833	1	1.540833	1.281941	0.308897	6.607891
	OLRs	133.7462	5	26.74923	22.2548	0.001988	5.050329
	Fault	6.009767	5	1.201953			
	Total	141.2968	11				

3.4. Other Parameters

Another negative effect of the increasing temperature on biological anaerobic treatment has been reported as poor sludge settling, resulting in high-effluent suspended solids, effluent turbidity and biomass washout (Gao *et al.* 2011). Therefore, in this study, effluent mixed suspended solid (MLSS) concentrations were measured under mesophilic and thermophilic conditions and found to be 141 mg/L and 152 mg/L, respectively. The small difference between the two temperatures was explained by the presence of a settling tank connected to the reactor. Furthermore, the sludge settleability was better at the optimum mesophilic temperature compared to the thermophilic treatment. As in the effluent phosphate concentration, the effluent ammonia concentrations were similar at both temperatures. Thermophilic conditions are known to cause poor settleability of sludge due to the deterioration of sludge settling properties (Abeynayaka & Visvanathan, 2011). However, this situation was tolerated by thermophilic anaerobic contact reactors, which are equipped with a settling tank.

4. Conclusions

In the present study, the applied maximum OLR was found to be higher under thermophilic conditions compared to the mesophilic treatment with the values being 8 kg COD/m^3·day and 5 kg COD/m^3·day, respectively. Accordingly, at lower HRTs, the thermophilic anaerobic reactor operated more effectively. Furthermore, the average methane production (0.42 m^3 CH$_4$/kg COD$_{removed}$) was found to be higher at the thermophilic temperature. Therefore, we conclude that the efficiency of thermophilic anaerobic treatment i325s higher than that of mesophilic anaerobic treatment. For future work, it is recommended that the reasons for the differences in the efficiency of anaerobic contact reactors be investigated by identifying anaerobic microorganisms at mesophilic and thermophilic temperatures.

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