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An Evaluation of Soft-drink Wastewater Treatment by Anaerobic Digestion Process

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ABSTRACT Series of batch operations were conducted for testing the suitability of anaerobic process for the treatment of soft-drink wastewater. No buffering control substances and biomass growth enhancer were added during the experiment although the wastewater used lacked those substances. Each batch operation resulted in the normal methane yield which was between 0.28 to 0.34 m^3 per kg COD removed. Nevertheless, with the increments of hydraulic loading up to one-third of the working volume, the treatment operation has unable to further remove the carbonaceous components. This failure was also shown by the cessation of CH_4 production. The final organic mass loading per working volume was at 1.33 kg/m^3, which was relatively low to cause failure. Further investigation showed that operation failed because of the methanogenesis process has been subjugated. Impediment of methanogenesis was caused by losses of its alkalinity during effluent withdrawal and addition of influent with low pH. VFAs were found to be as high as 1500 mg/L. Lack of nitrogen source was also the cause of the subjugation when reduction of biomass concentration were also had been observed. Treatment of such wastewater with low nitrogeneous substances and low levels of pH and alkalinity requires additional controlling measures to avoid operational failure.

ABSTRAK Beberapa siri operasi berkelompok telah dijalankan untuk menguji kesesuaian penggunaan proses anaerobik untuk rawatan air sisa minuman-ringan. Tidak ada bahan kawalan penimbal and penambah tumbesaran biojisim digunakan semasa eksperimen walaupun kedua-dua bahan ini adalah berkurangan dalam air sisa yang digunakan. Setiap operasi berkelompok telah menjanakan jumlah gas metana yang normal, iaitu diantara 0.28 hingga 0.34 m^3 per kg COD disingkirkan. Walaubagaimanapun apabila kenaikan muatan hidraulik meningkat sehingga satu per tiga dari jumlah isipadu kerja, operasi rawatan telah menunjukkan kegagalan untuk menyingkir komponen berkarbon. Kegagalan ini ditunjukkan oleh pengurangan penghasilan gas metana. Muatan organik per isipadu kerja yang terakhir adalah setinggi 1.33 kg/m^3, yang mana secara relatifnya adalah rendah untuk menyebabkan kegagalan operasi. Kajian seterusnya menunjukkan kegagalan operasi adalah disebabkan proses metanogenesis telah berhenti. Halangan proses ini adalah disebabkan oleh kehilangan alkaliniti semasa pemindahan keluar effluen dan penambahan influen yang mempunyai nilai pH yang rendah. Kehadiran VFA dengan kepekatan 1500 mg/L juga telah dicerap. Kekurangan sumber nitrogen juga menjadi penyebab kegagalan operasi apabila berlakunya pengurangan jumlah biojisim. Rawatan untuk air sisa yang kepekatan bahan bernitrogen, pH dan alkaliniti yang rendah memerlukan langkah kawalan tambahan bagi mengelakkan kegagalan operasi.

(Anaerobic process, soft drink wastewater, alkalinity, nitrogen sources, operation failures, volatile fatty acids)

INTRODUCTION

Water usage for the carbonated and non-carbonated soft-drink manufacturing operations has always been regarded to be high. Based on one of the case-studies reported in Japan [1], water consumption in soft-drink industry could reach as high as 4.3 ML/d, which is equivalent to 17,200 population equivalent (PE) of water supply at the consumption of water at 250 L/d per capita for developing countries in a tropical climate [2]. High consumption of water was contributed by the formulation of the soft-drink itself and also it is consumed by other sections of operations such as rinsing, washing, pasteurizing and cooling water. Wastewater recycling by this industry would be beneficial considering the fact that some processes in its operation do not require water with high purity grade. Treatment operation at lower financial constraint with high purification efficiency will encourage the recycling of water in such industries.

Biological processes for the treatment and recycling of wastewater have been considered cheap and environmentally sound. Theoretically, wastewater from soft drink industries should be biodegradable and can be treated by biological processes. Anaerobic digestion as one of the biological processes which was once considered as a strenuous process has been applied at the industrial scale [3]. It is able to receive high organic mass loading rate up to 2.3 kg/m^3/d and its ability to recover from a shock loading for anaerobic process is also high, depending on the bioreactor design and type of substrate [4].

The lack of attractiveness for this process is because of the misconception that it is an unstable operation and prone to failure. This is however conferred by misunderstanding the behaviour of the overall process. Anaerobic digestion process is known as a multiphase process which requires balance within the phases. This imbalance needs to be identified by conducting laboratory and pilot scale studies. It will be able to identify the inception of operational failures. In this study, anaerobic process was evaluated for the treatment of soft drink wastewater by batch operation at the laboratory scale. The evaluation did not include additional control techniques as it was designed for its failure. Determination of the causes of failures at laboratory scale will assist the outcome of preventive methods for the anaerobic process to be used in the actual scale.

MATERIALS AND METHODS

Soft-drink wastewater

Soft-drink wastewater was prepared by simulating the actual wastewater by dilution of fruit cordial so that the stock liquor contained vitamins and trace elements, as well as a carbon source. The dilution gave the concentration of wastewater up to 4000 mg/L of COD, which is in the range of medium strength wastewater [3]. Fibrous matter arises from the depulping process have been separated at the initial stage of production either by centrifugal process or water-presses, and managed under solid waste management. Selection of such substrate is to represent wash waters from industrial operation of fruit processing; i.e. pre washing of the fruit, cleaning of process vessels, pipelines and associated equipments [5].

Experimental set up

Batch operation was carried out after the working volume of 4L for continuous stirred tank reactor (CSTR) had been reached after the start-up operation. Before conducting the batch operation, the digestate from each reactor was mixed together and redistributed again in order to obtain a similar condition of seed sludge in all reactors. Production of CH_4 from the newly seeded sludge was monitored by running the operation overnight without substrate addition to assure the viability of anaerobic biomass. Acclimatization of the seed to soft drink wastewater began when the seed sludge stopped producing CH_4, which meant the sludge had stabilized and was ready to be used as the seeding.

The operation was conducted by triplicates of a 4L CSTR by batch operation. Reactors were submerged in the water bath at the temperature of 35°C. Each reactor was filled with 2L of digested sludge obtained form Southern Water Ltd., Millbrook, Southampton. Nitrogen gas was purged into the reactor for 10 minutes to remove the oxygen gas. Experimental set-up simulated the work of Borja and Banks [5].

Initial feed volume (FV) of 100 ml of substrate was fed daily to the reactor during the acclimatization process over a period of ten days. Subsequently, the daily feed volume increased to

250 ml, and increased to 500 ml. When the working volume reached four-litres, the acclimatization process recuperated for 24 hours. Experimentation began when its substrate had stabilized (zero production of CH_4). The volume of effluent to be withdrawn was equal to the volume of feeding volume to be introduced. Initially, 0.5L of substrate as feed volume (FV_1) was added and followed by 0.8L (FV_2), 1.0L (FV_3), 1.33L (FV_4) and 1.5L (FV_5). Each batch operation was running for 72 hours cycles. The withdrawal of the effluent was done by allowing the biomass in the reactor to settle. It would take two hours for the settling of the solid content and at the same time, the population of biomass in the system could be retained.

Chemical analyses

Chemical analyses were done according to APHA which included the analysis of chemical oxygen demand (COD), total solid (TS) analysis to represent biomass concentration, pH and alkalinity [6]. Measurements were done on the fresh substrate and mixed liquor from the reactor. Prior to COD analysis, sample of mixed liquor was first centrifuged to separate the solids. While for TS analysis, 50 ml of the digestate were taken and dried at 105°C for 24 hours. Measurement of biomass, pH and alkalinity, the analysis were performed on the mixed liquor of the digestate. Ammoniacal-N (NH_3-N) was measured using an ammonium potentiometry reference electrode, after the sample was being added with caustic chemical to pH of 12. Meanwhile, production of CH_4 was measured with a gasometer which collects the gas via volumetric liquid displacement.

Other series of analysis for the concentration and profile of volatile fatty acid (VFA) was also performed. VFAs were determined by GC using a 15m free fatty acid phase (FFAP) column packed with Chrom G (80 -100 mesh), together with a flame ionisation detector (FID). Oven temperature was programmed from 145 °C to 220 °C at a rate of 8 °C/minute. Nitrogen was used as the carrier gas at a flow rate of 30 cm^3/min. The samples were initially centrifuged at the speed of 20 000 rpm, acidified with 10% (v/v) formic acid and injected into the instrument. Composition of the VFA profiles were calculated according to the standard peaks provided by the known sample containing eight profiles of VFA from C_2-C_8.

RESULTS AND DISCUSSION

Wastewater characteristics

Simulated wastewater is useful as substrate strength can be manipulated to a predefined strength. Further analysis using gas chromatography showed no detectable VFA in diluted samples. The substrate was also free of suspended solids and NH_3-N substance. Because of the naturally acidity of fruit concentrate, when diluted, had a pH less than pH 4.0 with no measurable alkalinity.

Performance indicators

There are a few parameters that can be used to monitor the performance of anaerobic process operation, i.e. production of CH_4, removal of COD, pH, alkalinity and VFA content [7].

Production of CH_4 for all reactors had been recorded throughout the experiment as shown in Table 1. Cumulative production of CH_4 was measured intermittently. All FVs in Figure 1 shows the typical trend of CH_4 production rate. It describes CH_4 volumetric production (VP) rate based on the higher frequency of observation for cumulative CH_4 VP for each operation. Initial production rate was rapid and gradually decreased toward the end. Sharp changes for the rate were observed after the sixth hour. No CH_4 VP was recorded for FV_5 as there was no production of CH_4 had been observed.

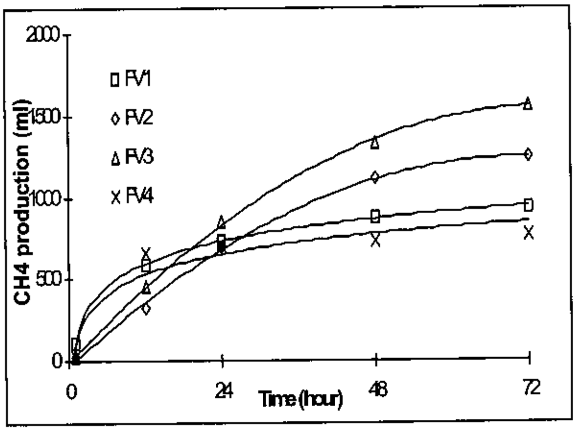

Figure 1. Cumulative CH_4 production during the 72 hours of batch operation for each batch operation

Cumulative CH_4 production increased with the amount of total organic mass loading, which was showed by COD content in Table 2. Nonetheless, volumetric production (VP) of CH_4 depends on the amount of organic content removed; it increased concurrently with COD removal as shown in Tables 1 and 2. Based on the cumulative CH_4 VP at FV_4, it indicated that the operation was beginning to stop removing organic content when lower CH_4 VP at the end of the experiment. This observation can be construed from Table 2 where lower COD removal was found with comparison to the amount of removal in FV_3. The production of CH_4 had completely ceased at FV_5 indicating that the operation had failed to remove organic substance from the system. Figure 2 shows CH_4 VP versus the amount of COD being removed. The slope value for each line explains the CH_4 yield. The range of CH_4 yield were from 0.28 to 0.34 (average of 0.32), which shows that the operation were operating in normal parameter based on the yield value [4, 7, 10].

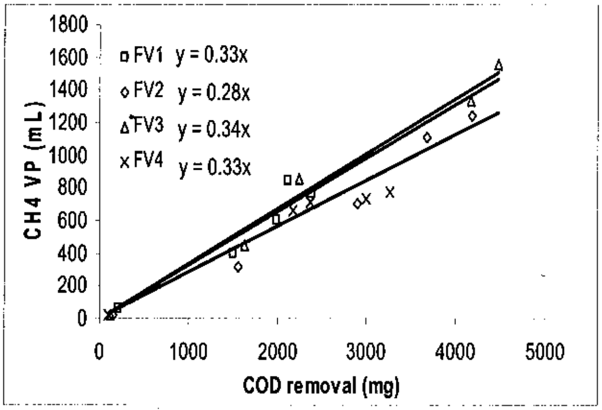

Figure 2. CH_4 VP versus COD mass removal for each batch operation

Table 2 shows COD content in the reactor for all FVs. Total mass of COD at time zero was calculated with Equation 1. Multiplying the unit of concentration (mg/L) with the unit of volume (L) shall cancel-off the volumetric unit (L) as left alone the unit of mass (mg). Theoretical value was taken at time zero as once the mixing of substrate started, COD removal would begin. COD mass removal at time intervals of 0, 1, 12, 24, 48, 72 hours for each series of FV. Total COD mass removal was calculated with Equation 2 while Equation 3 shows the calculation for total mass of COD at time = i by multiplying the concentration of digestate taken with the working volume. Equation 4 calculates the organic mass loading per working volume (OMLV), which uses COD as the organic matter. All [COD] measurements were referred to soluble organics, in order to emulate the removal of COD from the soft drink wastewater.

$$COD_{time=0} = \lfloor COD_{digestate} \rfloor \times V + \lfloor COD_F \rfloor \times FV$$

Equation 1

$COD_{time=0}$ (mg)	:	Total COD mass at time = 0
$[COD_{digestate}]$	:	Concentration of COD in reactor at time = 0 (mg/L)
V	:	Working Volume (L)
$[COD]_F$	:	Concentration of COD for each feeding regime at time = 0 (mg/L)
FV	:	volumetric feeding regime

$$COD_{removal} = COD_{time=0} - COD_{time=i}$$

Equation 2

$COD_{removal}$	:	Total COD mass removal (mg)
$COD_{time=0}$	:	Total COD mass at time = 0 (mg)
$COD_{time=i}$	:	Total COD mass at time = i (mg)

$$COD_{time=i} = [COD_{digestate}] \times V$$

Equation 3

$COD_{time=i}$	:	Total COD mass at time = i (mg)
$[COD_{digestate}]$	:	COD concentration in reactor at time = i (mg/L)
V	:	Working volume (L)

$$OMLV = \frac{COD_F}{V}$$

Equation 4

OMLV	:	Organic mass loading per working volume ($mg.L^{-1}$)
COD_F	:	Total COD mass in feeding regime-i ($[COD_F] \times FV$)($mg.L^{-1}$)
$[COD]_F$	:	Concentration of COD for each feeding regime at time = 0 ($mg.L^{-1}$)
FV	:	Volumetric feeding regime
V	:	Working volume (L)

Based on COD analysis, the minimum final discharge strength when treated by anaerobic process was about 300 mg/L COD except during

FV_4. It suggests that, the effluent should be further treated with other type of processes in order to comply with most of the exacting compliance. Final COD concentration at the time series during the FV_4 in Table 2 has shown that the operation has failed to reduce carbonaceous materials when the final concentration of COD remained at relatively higher concentration compared to FV_3 and FV_4. The operational failure was confirmed at FV_5 when the final [COD] remained at 2000 mg/L with zero production of VP-CH_4 at FV_5.

Table 1. Cumulative CH_4 production during batch operation for different FV

TIME (HOUR)	FV_1 (mL)	FV_2 (mL)	FV_3 (mL)	FV_4 (mL)	FV_5 (mL)
0	0	0	0	0	0
1	60	20	20	20	0
12	400	320	450	660	0
24	600	700	850	710	0
48	760	1110	1330	730	0
72	840	1240	1560	770	0

Table 2. [COD] in CSTR and total COD removal during anaerobic batch operation at different FV_i

	FV_1		FV_2		FV_3		FV_4	
TIME (HOUR)	[COD] mg/L	COD Removal (mg)	[COD] mg/L	COD Removal (mg)	[COD] mg/L	COD Removal (mg)	[COD] mg/L	COD Removal (mg)
0	820	0	1330	0	1400	0	1690	0
1	770	210	1320	50	1370	130	1670	100
12	460	1510	690	2560	1000	1630	1150	2170
24	400	1990	610	2900	850	2240	1110	2370
48	370	2380	420	3670	370	4160	950	3000
72	290	2120	290	4175	290	4470	890	3260

Organic mass loading per working volume (OMLV) at each FV_i per operation are as follows (based on Equation 4): 0.5 kg/m^3 (FV_1), 0.8 kg/m^3 (FV_2), 1.0 kg/m^3 (FV_3), 1.33 kg/m^3 (FV_4) and 1.9 kg/m^3 (FV_5). Failure at FV_4 with the volumetric organic loading of 1.33 kg/m^3 was unlikely to have contributed to the operational failures as the anaerobic process with the CSTR system can withstand higher loading [4]. In an UASB system, the OLMV could take up to 10.5 $kg/m^3/d$ without major changes in the performance [8]. It can be deduced that the environmental control system would be the contributing factors to this failure as the OLMV are considerably low, especially the feed substrate used in this experiment consist of simple substrates and easily biodegraded [5].

Due to the aspect of multiphase micro-organisms, failures in the operation were contributed by several other factors, such as pH, alkalinity, temperature and balance of nutrients [3]. Requirement for environmental factors for anaerobic process had been established, with pH within the neutral range, alkalinity levels from 1000 - 2000 mg/l, and operated in mesophilic range of micro-organisms [7]. Therefore further investigation proceeded to determine the cause of operational failures.

Figure 3 shows that the treatment operation was not able to sustain the microbial population in the reactor, as the biomass concentration decreased rapidly from 13,000 mg/L to 8000 mg/L for each increment of hydraulic volumetric removal. It also suggests that the biomass yield was too low to replenish the biomass which was flushed out from the system via hydraulic removal. This could be due to zero concentration of NH_3-N^+ as the nitrogen source for the system. A portion of the methanogen population could have been "self-digested" through the hydrolysis phase when the ceased to function. In anaerobic digestion, the primary processes (hydrolysis and acidogenesis) and the conversion of the acid products by acetogenic and methanogenic bacteria into CH_4 and CO_2 [9], whereas the dead bacteria will be foraged by others [3].

pH, Alkalinity and VFA

Low pH level was the major factor which contributed to the failure of anaerobic operation at the highest COD mass load (FV4). The recommended pH range for an anaerobic methanogenic reactor is between pH 6.5 - 7.5 for optimum performance [10]; at FV_4, the pH level dropped below than pH 6.0 which is shown in Figure 4. Although, the pH recovered to 6.3, but subsequently, it had dropped to pH of 6.2. It is well known that methanogenic activity is more likely to proceed optimally in a narrow pH value range, between 6.3 and 7.8 [11].

The effect of a drastic pH-change during the operation depends on the available alkalinity in the reactor. Further analysis on the mixed-liquor chemical characteristic showed that the pH dropped because of low alkalinity in the reactor. Buffering capacity had been reduced following each increment of FV into the system, as shown in Figure 5. The alkalinity had dropped from 2300 mg/L $CaCO_3$ to 1000 mg/L $CaCO_3$. This shows that each increment of FV had reduced the alkalinity level. Maintaining alkalinity at a higher level would have helped to reduce the acidifying effect of VFA during the early stages of acidification. This can be observed during the first 12 hours of batch operation where there is a noticeable drop in pH and alkalinity during this time (Figure 4 and 5). The reactors recovered from this in those receiving a lower mass load (FV_1 to FV_3) where a rise in pH after 24 hours was observed. According to a study with sugar beet wastewater, process efficiency recovers almost immediately from pH shocks once the influent pH is returned to the optimal range [12]. In the case of sudden changes of pH, the recovery of the process could take place depending on the extent and duration of the imposed change, as well as on the concentration of VFA during the event. However, at FV_4 all the reactors turned "sour" and continued to produce lesser CH_4 at the pH of 5.7. After 24 hours, the operational pH had increased back to pH 6.0, however full recovery was not taking place as [COD] remained high (above 900 mg/L) with small increment of CH_4 VP till 72 hours. It shows that the methanogen has been impeded by either low pH or VFA toxicity.

Table 3 shows the concentration of VFAs and its components in the "soured" reactor at 72 hours cycle of FV_4. Total VFAs had reached up to the concentration of 1500 mg/L and each of VFA profile shows that the process of acidogenesis and acetogenesis did take place, however, methanogenesis had not. This could be indicated by the high accumulation of acetic acid and followed by higher length of other VFAs. Methanogen bacteria are known to be susceptible to low pH and higher concentration of VFA with longer carbon chain than acetic acid [12].

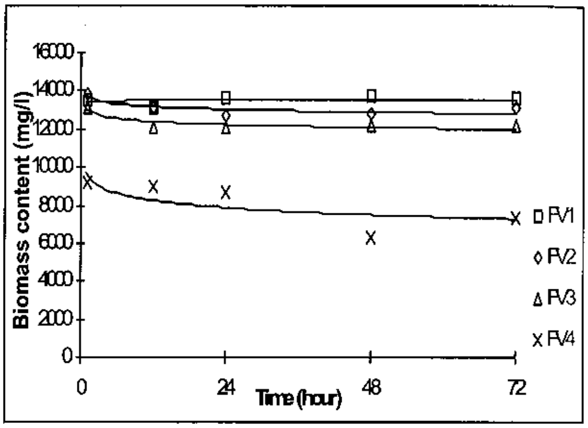

Figure 3. Biomass concentration during the 72 hours of batch operation for each batch operation

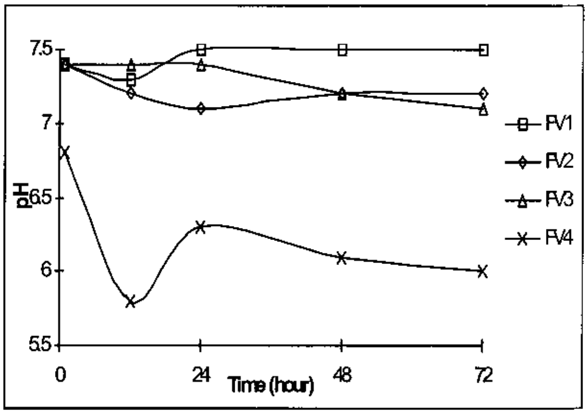

Figure 4. pH level during the 72 hours of batch operation for each feed volume

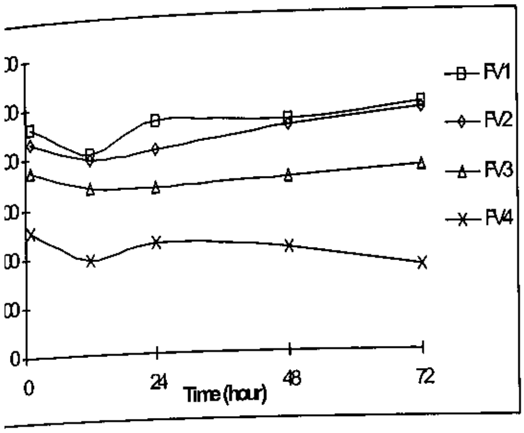

Figure 5. Alkanity level during the 72 hours of batch operation for each feed volume

VFA can be used as the process indicator. Presence of butyrate and isobutyrate at the end of FV_4 shows that the treatment operation has been perturbed with similar finding by Ahring *et al.* [13] who used VFAs as the indicator of process imbalance. In comparison to the use of manure as a substrate, it was shown in a batch experiment that VFA at concentrations up to 100 mg/L did not reduce the overall methane production rate [13] Thus, much higher concentration of total VFA in this experiment has supported the deduction that imbalance process of non-methanogen and methanogen had occurred.

Table 3. Total Concentration of Volatile Fatty Acids and its components at end of FV_4 cycle

COMPONENTS	CONCENTRATION (mg/L)
Total VFAs	1500
Acetate	500
Propionate	100
Butyrate	110
- iso butyrate	10
- n butyrate	100
Valerate	110
- iso valerate	10
- n valerate	100
Caproate	50

CONCLUSION

This study has shown that in the application of anaerobic batch operation for the treatment of soft drink wastewater, the alkalinity and pH levels during the first 12 hours should be closely monitored especially with higher organic mass loading. To use anaerobic digestion process for the treatment of soft-drink wastewater with low alkalinity, pH and nitrogen sources requires further controlling approaches. Without the controlling mechanism for pH control and sustaining the biomass and its population, failures to remove the carbonaceous substances from the wastewater would occur. Failures can be set off by a sudden drop of pH and accumulation of VFA, which would affect the methanogen population of bacteria to transform acetic acid into CH_4. Imbalance of population between methanogen and non-methanogen has further instigated the accumulation of VFAs in the system and perturbs the treatment operation.

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ABBREVIATIONS

COD	: chemical oxygen demand
CSTR	: continuous stirred tank reactor
VFA	: volatile fatty acid
VS	: volatile solids
VSS	: volatile suspended solids
CH_4	: methane
FV_i	: Volumetric feeding regime at series-i (mL)
PE	: population equivalent
L	: litre
OMLV	: organic mass loading per working volume
[ ]	: concentration (mg/L)
VP	: methane volumetric production (mL)
TS	: total solid (mg/L)
T	: time