Effect of particle size on mesophilic anaerobic digestion of thermally pre-treated waste activated sludge

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The objective of this study was to demonstrate a significant difference in the rate of methane production when anaerobic digestion of sewage sludge is done using different particle sizes. To this end, several parameters were determined in thermally pre-treated waste activated sludge at different temperatures: floc disintegration energy, efficiency of solubilisation and production rate of methane. Energy disintegration was 3,232 kJ/kgTS, the best solubilisation efficiency (26%) was observed when the waste activated sludge was heated to 90°C. Particle sizes tested were 105, 74, 62, 53, 37, 16, 8, and 2.2 µm. The maximum methane production rate (0.21 kg $CH_4/m^3/d$) was obtained with the smallest particle size. There are significant differences between methane production rates particle sizes.

Keywords: particle size; sludge; anaerobic digestion; energy disintegration.

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Abbreviations: COD - Chemicals Oxygen Demand; EPS - Extracellular Polymeric Substances; PS - Primary Sludge; SS - Suspend Solids; TS - Total Solids; TSS - Total Suspend Solids; VS - Volatile Solids; VSS - Volatile Suspend Solids; WAS - Waste Activated Sludge; WWTP - Wastewater Treatment Plant.

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Introduction

Large amounts of biomass, commonly called sewage sludge, are generated as by-products during the operation of municipal wastewater treatment plants. In Mexico, 3,201 tons of daily sewage sludge [1] is produced in average, and it is estimated that about 90% of sewage sludge generated in wastewater treatment plants is discharged without any treatment to the sewage system in water bodies or disposed of in landfill, causing pollution of surface water, groundwater and soils and generating public health problems.

For the disposal of sewage sludge it is necessary to stabilize it, that is, to reduce the volume, and the amount of organic matter and pathogens. Biological processes present a viable alternative for stabilization because, unlike the physicochemical processes, the stabilized sludge can be reused.

The digestibility of waste activated sludge (WAS) is considerably less than that of the primary sludge (PS). Biodegradability of the lower WAS has been attributed to the recalcitrant nature of various cellular components such as bacterial cell walls and extracellular polymeric substances (EPS) that are part of aerobic floc. This feature of low biodegradability has focused on WAS study sewage sludge stabilizing them.

Mesophilic anaerobic digestion has long been used to treat WAS. The methanogenic process is limited by the hydrolysis rate of organic suspended matter [2, 3], which requires anaerobic reactors to be operated with solids retention times greater than 20 days [4, 5, 6]. By improving the hydrolysis step, organic matter becomes more available to anaerobic bacteria, accelerating the digestion, increasing the volume of biogas produced and decreasing the solids retention time in the digester.

For this reason the use of mechanical, chemical and biological pre-treatments has been proposed to accelerate the solubilisation step and hydrolysis of the suspended solids (mainly consisting of proteins, carbohydrates and lipids). Pre-treatments have shown good disintegration efficiencies. However, there has been a significant increase in the degradation rate and retention times in the anaerobic reactors, which remain in the order of 20 days, even after pre-treatment [7]. A hypothesis that may explain this behavior in anaerobic digestion of WAS is the heterogeneity of the particle size generated during pre-treatment. Some studies show that the particle size distribution of the suspended solids causes an increase in methane production [8]. In this context, the aim of this study was to determine the effect of particle size on the rate of methane production in mesophilic anaerobic digestion of thermally pre-treated WAS.

Materials and method

Waste activated sludge

WAS from the Wastewater Treatment Plant (WWTP) (Tecámac, México), which treats 170 L/s of wastewater, was used. The conventional wastewater treatment used in these plants consists of preliminary (sieving and sand trap) and secondary treatment in the activated sludge unit. The collected WAS was consolidated by sedimentation in a pipe of 15.3 cm diameter and 207 cm long, for 24 h. Once consolidated, the sludge (total solids concentration about 3±0.5%) was stored in polypropylene bottle at 4°C.

Waste activated sludge composition

To know the characteristic of the WAS, total (TS) and volatile solids (VS) concentrations in all samples were determined by heating at 105°C during 24 h for total solids and at 550°C during 2 h for volatile solids. Soluble fractions of the sludge were defined by centrifuging at 3,500 rpm for 15 min. The organic matter concentration was measured as chemical oxygen demand (COD) by closed reflux method, all according to APHA [9]. Carbohydrate and protein were determined according to the method of Delgenès [10].

Thermal treatment

Samples of 250 ml of WAS were subjected to the following temperatures 55, 60, 70, 80, and 90°C. Heating was conducted in a temperature controlled oil bath. The heating time was corresponds to that required to reach the desired temperature, and the cooling period corresponds to the time it took WAS to reach 35°C. Once cooled the solubilisation degree (SD) of COD was calculated according to equation 1.

$$\%S_D = \frac{CODs_{treatment} - CODs_0}{COD_{total} - CODs_0} \qquad (1)$$

Where, $CODs_{treatment}$ is the soluble COD after the thermal treatment. $CODs_0$ is the soluble COD in the WAS before treatment, COD_{total} is the total COD in the sample, all expressed in g/L.

Particle size

A sample of 50 ml of raw and thermally treated WAS was screened by using the following particle sizes: 105, 74, 62, 53, 37, 16, 8, and 2.2 µm. The mass of particles retained on each sieve was measured by weight difference. The filter cake was recovered by backwash with 50 ml distilled water.

Calculation of disintegration energy

The floc disintegration step is considered as a first order reaction (equation 2).

$$\frac{dSS}{dt} = k[SS] \quad (2)$$

Where SS is the concentration of the suspended solids (g/L), t is the time in minutes, and k is the rate constant of the first order per min.

To determine the value of k at different temperatures, we integrated equation 2 and obtained equation 3.

$$\ln\frac{SS}{SSo} = kt \quad (3)$$

The slope of the plot of ln (SS/SSo) vs. time is k. The Arrhenius equation (equation 4) is linearized (equation 5) to determine the decay energy (E) represented by the slope of the plot of ln (k) vs. 1/RT.

$$k = Aexp\left(\frac{-E}{RT}\right) \quad (4)$$

$$\ln(k) = lnA - \frac{E}{RT} \quad (5)$$

Inoculum

The inoculum used in an anaerobic sludge reactor was a UASB (up flow anaerobic sludge blanket, designed and manufactured in the laboratory of anaerobic technology. Technology of Advanced Studies Ecatepec, México) at 8.5 L, operated at 35°C with 12 h of hydraulic retention time (HRT). RAMM medium was fed [11] with glucose as carbon source and pH 7.0 ± 0.05.

Kinetics of anaerobic biodegradability

Biodegradability tests were carried out in reactors of 120 ml total volume, with 80 ml working volume. During the experiment, a blank solution always considered for quantifying the hydrolysis of inoculum. The volume of methane produced in the blank was subtracted from that obtained in biodegradability tests. The substrate was WAS thermally pre-treated sludge, and nutrient enriched RAMM medium. The initial substrate concentration in all experiments was of 3.5 g COD/L. Inoculum concentration was at 1.5 g VSS/L under mesophilic (35°C) conditions.

To evaluate the effect of particle size on the biodegradability of thermally pre-treated WAS, kinetics anaerobic biodegradability test was carried out to compare methane production for different size particle diameters, >105, 74, 62, 53, 37, 16, 8, and <2.2 µm, respectively. Specific methane production rate was calculated using equation 6.

$$r_{CH4} = \frac{Q_{CH_4}}{V_r} \times \frac{16}{22.4} \quad (6)$$

Where r_{CH4} is the methane production rate (kg $CH_4/m^3/d$), Q_{CH4} is accumulated volume methane (STP) (m^3/d), V_r is the reactor volume (m^3). 16 is the molecular weight of methane (16 kg/kg-mol) and 22.4 are the volume occupies for a kg-mol of gas (m^3).

Biogas volume was quantified by a column displacement of saturated sodium chloride (pH 3.5) contained in a glass tube of 3.5 cm diameter. The biogas composition was determined by taking a sample from the collector biogas reactor and injecting 0.1 ml into a gas chromatograph GOW-MAC Instrument Co, U.S.A. with an SP-4290 integrator and a stainless steel column packed with carbosphere. The operating conditions of the gas chromatograph were: injector temperature, 170°C; column temperature, 140°C; detector temperature, 190°C; helium was used as carrier gas with a flow of 30 ml/min. Filament current was 120 mA.

Analysis Statistical

An experiment with 8 levels of particle size was designed to determine the influence of anaerobic degradation WAS. The interest is to compare all pairs of treatment means using analysis of variance. Tukey's test states that two means are significantly different if the absolute value of their sample differences exceeds a distribution t (Tα) with a scale factor, involving the mean square error, $(MS_{E/n})^{1/2}$ (equation 7):

$$T_\alpha = q_\alpha(a,f)\sqrt{\frac{MS_E}{n}} \quad (7)$$

With a global significance level of 0.05 (α), eight levels (a), four repetitions (n), and 24 degrees of freedom (f).

Results and Discussion

Characterization of waste activated sludge

The composition of the waste activated sludge (WAS) used as substrate is pH 7.06, TS 27, VS 21, TSS 26, VSS 20, COD 26.8, carbohydrates 4.5, and protein 16.5, all of them in g/L. The COD_{total} represents 99.25% of the TS. The volatile solids (VS) account for 77.77% of TS. With the total suspended solids (TSS) non-soluble materials were quantified, representing 96.29% of the TS in the sample of WAS, this implies that most of the substrate, which can be exploited by microorganisms during anaerobic digestion, must first be solubilized.

WAS is composed mainly of carbohydrates and proteins, their content has been reported, with respect to the TS, in the range of 44 to 54.2% for proteins and of 7.5 to 1.68% for carbohydrates [12]. The sludge analyses here contained 16.55% carbohydrate and 60.92% proteins with respect to the TS.

Waste activated sludge solubilisation

In this study, the term "solubilisation" was used to describe the transfer of suspended solids from the liquid fraction after the heat pre-treatment of WAS. Temperature-time profile during pre-treatment is shown in figure 1; 95% solubilisation of the suspended solids is achieved during the heating step and the rest during the cooling step. Table 1 shows the effect of temperature on the solubilisation of WAS. The solubilisation obtained for COD (16.8 to 26.1%) is in the range reported in other studies [13, 14]. Similarly, solubilisation of volatile suspended solids (VSS) increases with temperature going from 7.3% at 55°C to 26.7% at 90°C, these values are in the range reported for similar temperatures. For example, Bougrier et al. and Kim et al. [13, 8] reported a solubilisation of 19% and 10% respectively, for WAS pretreated at 121°C for 30 minutes.

Table 1. Effect of temperature on solubilisation of WAS.

Temperature	% Solubilisation	
°C	COD	VSS
55	16.8	7.3
60	17.1	5.3
70	18.3	16.0
80	22.8	20.0
90	26.1	26.7

Calculation of decay energy

In equation 2 the concentration of suspended solids (SS) represents the flocs in the WAS and (k) is the first order constant. k was used to calculate SS solubilisation kinetics. The rate constant of the first order was calculated by linear regression of ln (SSt/SSo) versus time at different temperatures (figure 2).

Decay energy (E) was calculated by linear regression of ln (k) against the reciprocal temperature. The slope of figure 3 represents E, so the decay energy floc is 19,317 cal/mol. This energy is below that necessary to inactivate a microorganism (79,000 cal/mol) [15]. This may explain the apparent recovery of pathogenic microorganisms in pre-treated WAS observed in other studies [16, 17]. This reactivation may imply that the bio-solid does not comply with the maximum permissible limits.

Whereas the empirical molecular formula of

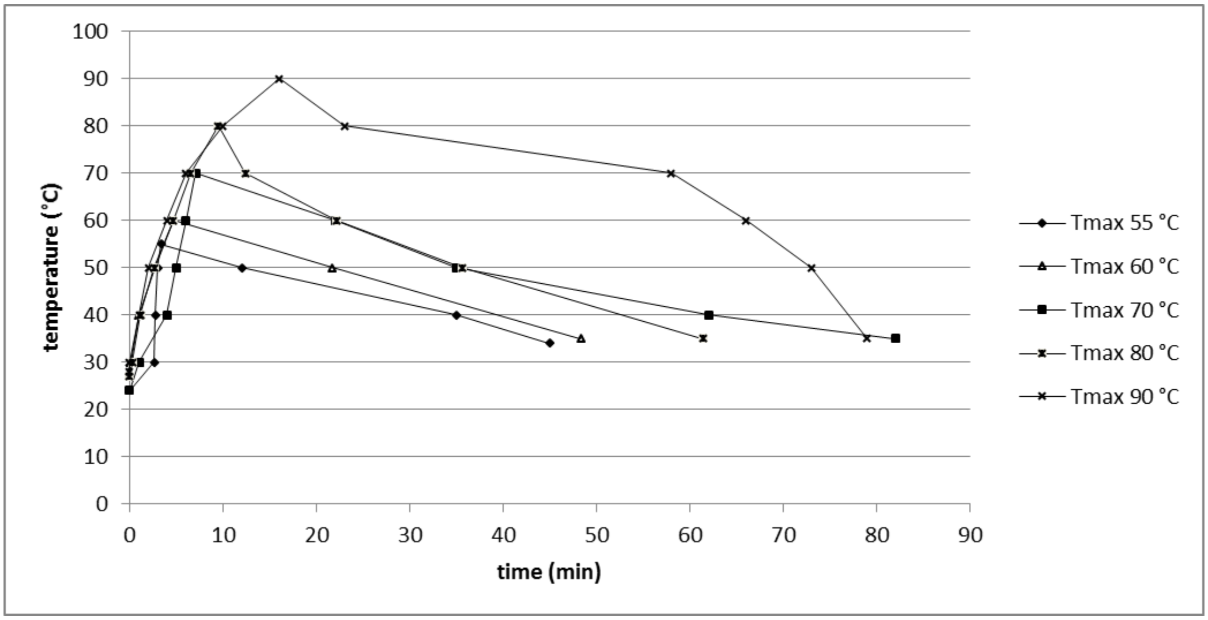

Figure 1. Time-temperature profile for thermal pre-treatment of WAS.

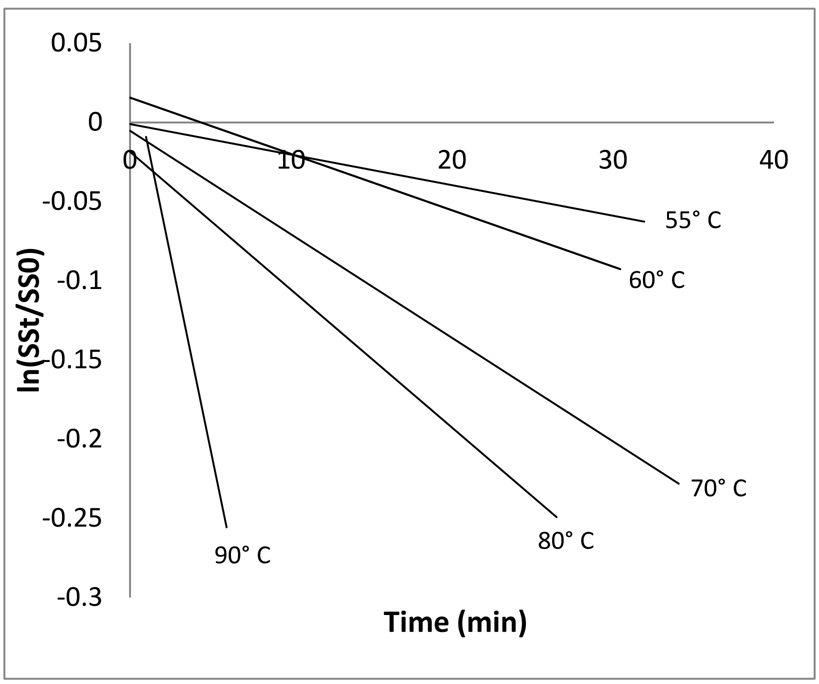

Figure 2. Rate constant (k) at different temperatures.

VSS is $CH_{2.53}O_{0.430}N_{0.247}S_{0.004}$ [18], this decay energy corresponds to 3,232 kJ/kg TS and the order of magnitude agrees with that reported by other authors [19, 20]. Hence total disintegration of the SS seems to be dependent on the effective implementation of energy and separation stages of the dissolved solids, in order to promote a complete disintegration of the SS with minimal energy use.

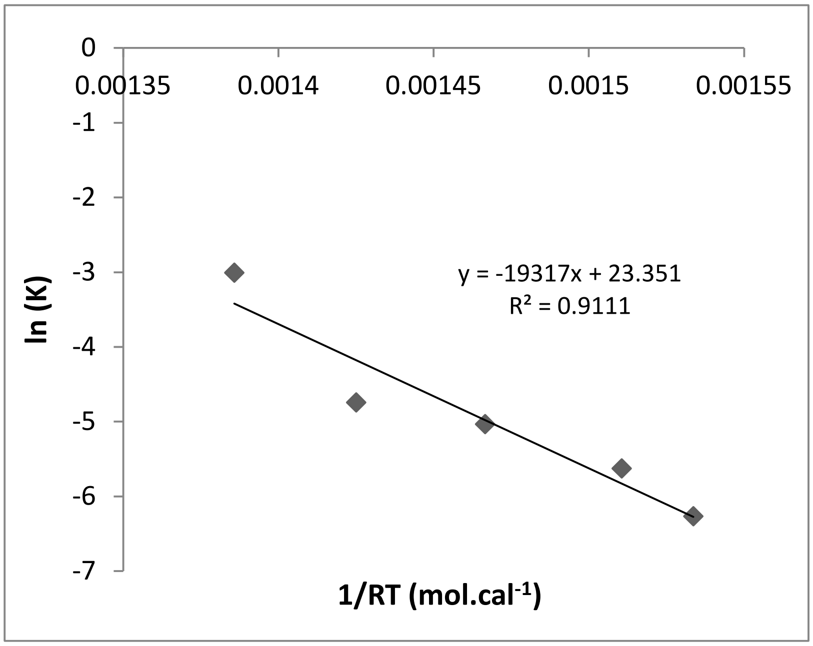

Figure 3. Linearization of Arrhenius equation to determine the floc disintegration energy in WAS.

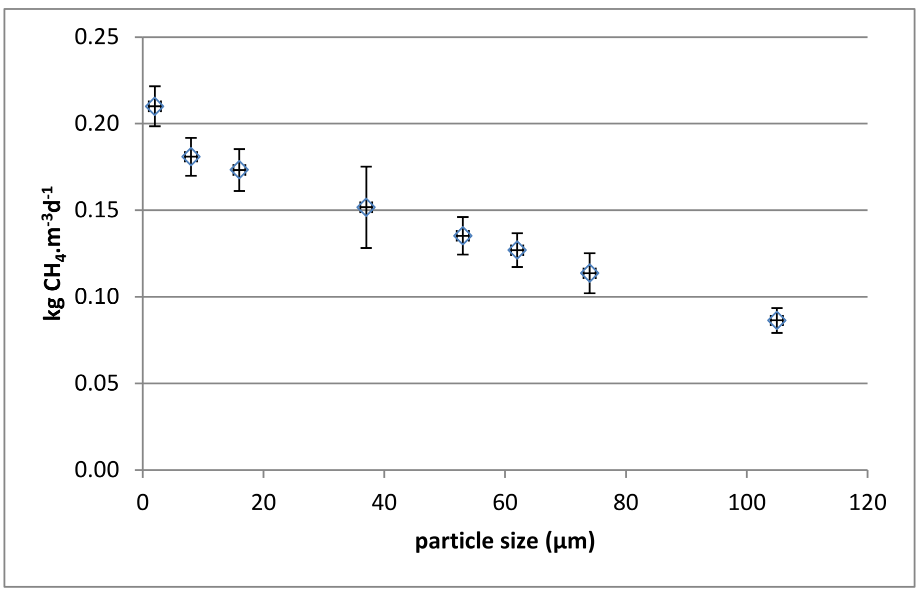

Figure 4. Kinetics of thermally pre-treated WAS pre-treated at 90 °C with different particle sizes.

Effect of particle size on the rate of methane production

To evaluate the effect of particle size on the rate of methane production, using as substrates the solids from the thermally pre-treated WAS, methane production kinetics was assessed. The anaerobic sludge used as inoculum for the kinetics had a methanogenic activity of 0.32±0.05 g COD_{CH4}/g VSS/d. Granular sludge anaerobic methanogenic activity between 0.5 and 1.5 g COD_{CH4}/g VSS/d are reported [21].

Figure 4 shows the trend of the rate of methane production by different particle sizes, the

Table 2. Tukey´s test for the average rate of methane production in anaerobic digestion of thermally pre-treated sewage sludge.

Particle size (µm)	average $kg\ CH_4.m^{-3}d^{-1}$	desv est $kg\ CH_4.m^{-3}d^{-1}$	S^2	$S^2*(n-1)$	
105	0.09	0.007	5.07E-05	1.52E-04	a= 8
74	0.11	0.012	1.52E-04	4.55E-04	N = 32
62	0.13	0.010	5.25E-04	1.58E-03	n = 4
53	0.14	0.011	3.73E-04	1.12E-03	f = 24
37	0.15	0.023	1.33E-04	4.00E-04	SS_{E} = 5.34E-03
16	0.17	0.012	1.88E-04	5.65E-04	MS_{E} = 2.23E-04
8	0.18	0.011	2.48E-04	7.43E-04	$q_{0.05}$ (a,f)= 4.68
2	0.21	0.012	1.10E-04	3.31E-04	T = 3.49E-02

Table 3. Absolute value of the difference between the means of the production rate of methane and different particle sizes.

Δyi	abs(Δyi)	Δyi	abs(Δyi)	Δyi	abs(Δyi)
y6-y7	7.62E-03	y6-y8 *	3.67E-02	y2-y6*	5.97E-02
y2-y3	1.33E-02	y3-y5 *	3.80E-02	y1-y5 *	6.53E-02
y3-y4	1.64E-02	y4-y6 *	3.80E-02	y2-y7 *	6.73E-02
y4-y5	1.64E-02	y2-y5 *	3.81E-02	y3- y7 *	7.47E-02
y5-y6	2.16E-02	y1-y3*	4.06E-02	y4-y8 *	7.47E-02
y2-y4	2.16E-02	y3-y6*	4.56E-02	y1-y6*	8.69E-02
y1-y2	2.73E-02	y4-y7 *	4.56E-02	y1-y7*	9.46E-02
y7-y8	2.91E-02	y1-y4*	4.89E-02	y2-y8 *	9.64E-02
y5-y7	2.92E-02	y5-y8*	5.83E-02	y1-y8*	1.24E-01
				y3-y8 *	1.35E-01

Yi = 1:105 µm, 2:74 µm, 3:62 µm, 4:53 µm, 5:37 µm, 6:16 µm, 7:8 µm, 8:2.2 µm

maximum rate of production of methane occurred when the particle diameter was less than 2.2 µm and a decreased rate of methane production was observed with increasing particle size. By comparing pairs of means of methane production rates of various particle sizes (Tukey's test, table 2), it was determined that there is significant difference between the difference r_{CH4} with increasing particle size (table 3). Column abs (Δyi) in table 3 shows the absolute value of the difference among the means of the different particle sizes, this difference is compared with the value of T (table 2), if the difference is greater than T then there is a significant difference among means (asterisked). These data show that the difference between the particle sizes and the rates of methane production will be significant. This may imply that the rate of methane production is a function of particle size, in the range tested. The rate of methane production for smaller particle sizes, where digested anaerobically pretreated WAS: 0.15 to 0.30 kg $CH_4/m^3/d$ [22, 23]. It seems that the surface of the substrate plays an important role in the hydrolysis of particulate substrate. This fact agrees with the results obtained by other researchers in the generated evidence that the hydrolysis process of particulate substrate this related to the particle size of the particles or the number of adsorption sites at the particle surface. Moreover, microscopic observations showed the substrate particle in a digester are immediately colonized by bacteria which secrete extra-cellular enzymes. Other studies showed that 50% of the enzyme activity this strongly bound to the sludge [24]. The result above lead to the idea that mechanism exist the release of enzymes and the subsequent hydrolysis of the particle is described by Batstone [25] in where the organisms attaches to the particle, secretes enzymes into the vicinity of the particle and next the organism will benefit from the released dissolved substrates.

Conclusions

Decay energy of the floc was 19,317 cal/mol, this energy is less than that required to inactivate a microorganism (79000 cal/mol), implying that the stabilized bio-solids could not meet the specification for pathogens, established in Mexican norm (NOM-004-SEMARNAT-2002).

The decay energy corresponds to 3,232 kJ/kg TS similar to that reported when the pretreatment value is ultrasound, which may imply that the total disintegration of the SS seems to be subject to the effective implementation of energy and separation stages dissolved solids to promote a complete disintegration of the SS with minimal energy use.

The particle size has significant effects on the rate of methane production as differences among means revealed that the difference between particle sizes and the rates of methane production is significant.

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