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Short Communication

Drinking water treatment sludge as an effective additive for biogas production from food waste; kinetic evaluation and biomethane potential test

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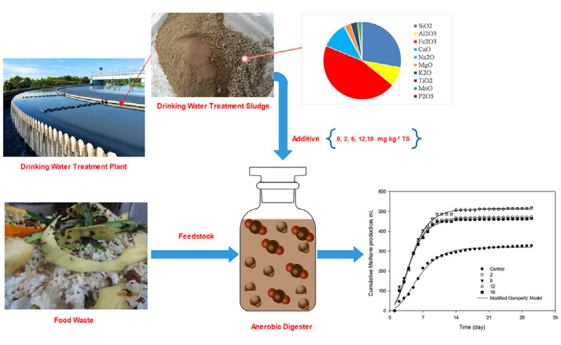
GRAPHICAL ABSTRACT



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ABSTRACT

The effect of drinking water treatment sludge (DWTS) as a mixture additive, on biogas and methane production from food waste was studied. Mesophilic anaerobic digestion of food waste with 5 concentrations of DWTS (0, 2, 6, 12, and 18 ppm) was carried out. It was found that DWTS can significantly enhance biogas and methane yield. The highest biogas (671 Nml/g VS) as well as methane yield (522 Nml/g VS) was observed when 6 mg/kg DWTS was added. This is equal to 65 and 58 percent increase in comparison with the control digester. The calculated lag time for methane was found to be in between 3.3 and 4.7 days. The DWTS also reduced the lag phase and retention time. The biogas experimental data was fitted with the modified Gompertz and the first-order kinetic models with R^2 higher than 0.994 and 0.949, respectively. The ratio of the experimental biogas production to the theoretical biogas production (ε) for control sample was 0.53 while for other samples containing additive were higher than 0.78.

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1. Introduction

To enhance the economy of a biogas plant, which is achieved by increasing biogas yield, different approaches have been investigated. In this regard, Co-digestion, pretreatment, development of new reactors configurations, and using additives to stimulate the bacteria growth and decrease inhibitory effects are of those interesting techniques (Ahmadi-Pirlou et al., 2017). In AD of food wastes which have low concentration of trace elements, addition of micronutrients is even necessary (Xu et al., 2018). It has been identified that micro and macro nutrients can stimulate methane production and the process stability (Demirel and Scherer, 2011). Trace elements have been proven to stimulate methane production at a certain concentration range above which, inhibition occurs (Lo et al., 2012). Most of the studies have examined the effects of addition of one or two metals on biogas production while there might be antagonistic or synergistic effects between some elements (Romero-Güiza et al., 2016). Only a few studies have dealt with the effect of a mixture of various trace elements on the performance of anaerobic digestion. Recently, Menon et al. (2017) reported 50% increase in biogas yield from food waste by adding a mixture of Ca, Mg, Co and Ni. Similarly, Voelklein et al. (2017) could obtain a stable process at high loading rate in the presence of a mixture of Co, Fe, Mo, Ni and Se. In spite of the positive impacts of trace elements, its use in large scale is limited mostly due to the high cost of such chemicals. Therefore the use of a cheaper source of micro nutrients can make it more economically feasible (Huiliñir et al., 2015). In this regard, successful use of fly ash was reported by Huiliñir et al. (2017) and Huiliñir et al. (2015).

Nevertheless, to the best of our knowledge, no research has been published so far, investigating the possibility of improving biogas yield through the addition of drinking water treatment sludge (DWTS). DWTS is a mixture of alkaline, trace, heavy metals, and clay produced during the treatment of surface water for drinking usages. Currently it is considered as a waste, which should be somehow disposed of (Ahmad et al., 2016). Therefore, the aim of the present project was to assess the feasibility of improving biomethane yield from AD of food waste.

2. Material and method

2.1. Materials

Food waste sample was taken from the canteen of Ferdowsi University of Mashhad, Iran. Cooked food (e.g. rice and meat), vegetables (e.g. parsley, chives basil, cabbage and lettuce), and bread were the components of the sample. The garbage was prepared over a three-day period and stored at −20 °C. DWTS was collected from a drinking water treatment plant located in Mashhad, Iran. Before use, the sludge was air dried, grinded, and then calcinated at 550 °C for 2 h. Sodium dodecylbenzenesulfonate and Cellulose were purchased from Merck and Sigma-Aldrich Company, respectively.

2.2. Experimental design

Biomethane potential tests of food waste were performed in a batch anaerobic system under mesophilic conditions. Glass bottle with a working volume of 350 mL were used as bioreactor. Anaerobically digested food waste from a continuous bench scale lab reactor in steady state operation was used as inoculum. The inoculum to substrate ratio was adjusted to 2:1 based on VS. The properties of food waste and inoculum are given in Table 1. The DWTS was added to reactors based on method proposed by (Kaluža et al., 2014) as follow: 0.01 g of DWTS was dispersed in 100 mL of distilled water under stirring and then 0.0001 g sodium dodecylbenzenesulfonate was added to enhance metal suspension . From this solution, different concentrations of DWTS (0, 2, 6, 12, and 18 mg/L) were prepared for AD experiments. These experiments were named as S_0, S_2, S_6, S_{12}, and S_{18} respectively. For the viability of biomethane potential test, positive control experiment with microcrystalline cellulose (Sigma-Aldrich) was carried out. The biogas from each reactor was collected separately in a Tedlar Bag as long as the daily produced biogas was less than 1 percent of the total yield. The biogas volume was determined through evacuating the bag by a 60 mL graded syringe, and measuring the volume necessary for it to be completely emptied Naran et al. (2016) and Kim and Kang (2015). All experiments were run in triplicate and the average was reported.

Table 1
Chemical composition of food waste.

Parameter	Food waste	Inoculum	Cellulose
TS (%)	41	4	95
Moisture content (%)	59	–	–
VS (%)	91	60	92
Nitrogen (%)	2.8	–	–
Carbon (%)	43	–	–
Hydrogen (%)	5.28		
Oxygen (%)	48.92		
C:N ratio	15.3	–	–
pH	7.1	7.3	–
S (ppm)	2485		
P (ppm)	1451		

2.3. Analytical method

The bio-methane content was determined using Einhorn fermentation-saccharometer as described previously with details by Zeynali et al. (2017) and approved by Kaluža et al. (2014). The total solid (TS) and volatile solid (VS) were measured according to standard methods (EPA-821-R-01-015, 2001). Carbon, nitrogen, hydrogen and sulfur content of the food waste were determined by CHNS Elemental Analyzer (Costech ECS 4010, Italy). The oxygen content of the sample was determined by subtracting the sum of carbon, nitrogen and hydrogen percent from 100. The pH value was measured by a digital pH meter (pH-201 Lutron, Taiwan).

2.4. Kinetic evaluation

The methane production can be predicted by Pseudo first-order kinetics model (Al Seadi et al., 2008):

$$G_t = G_0 \times (1 - e^{(-kt)}) \tag{1}$$

where G_t is the volume of cumulative methane (L/kg TS) at digestion time t (days); G_0 is the maximum volume of methane (L/kg TS); k is the methane production rate constant (day^{-1}). In order to determine the efficiency of AD, the duration of the lag phase is also an important parameter. The modified Gompertz model can be used to calculate the lag phase as follows:

$$G_t = G_0.\ exp\left\{-\exp\left[\frac{R_{max}.\ e}{G_0}\right](\lambda - t) + 1\right\} \tag{2}$$

where R_{max} is the maximum methane production rate (L Kg^{-1} TS-d); λ is the lag phase (day); t is time (day), e is exp(1) = 2.7183. A nonlinear regression analysis was performed using SigmaPlot software, version 12.3 to calculate the kinetic constants.

2.5. Theoretical biogas production

Theoretical biogas and methane productions were calculated based on Buswell formula (Buswell and Neave, 1930):

$$C_aH_bO_cN_d + \left(\frac{4a - b - 2c + 3d}{4}\right)H_2O \rightarrow \left(\frac{4a + b - 2c - 3d}{8}\right)CH_4 + \left(\frac{4a - b + 2c + 3d}{8}\right)CO_2 + dNH_3 \tag{3}$$

Table 2
The composition of DWTS based on XRF results.

Components	Quantity (wt%)	Elements	Quantity (ppm)
SiO_2	24.51	Ba	749
Al_2O_3	7.01	Co	93
Na_2O	0.4	Cr	127
MgO	2.22	Nb	6
K_2O	2.47	Ni	89
TiO_2	0.45	Zr	107
MnO	1.03	Cl	990
CaO	9.61	Zn	1803
P_2O_5	0.38	Rb	75
Fe_2O_3	39.96	Sr	282
LOI	11.17	V	123
		Y	14
		S	1283
		Ce	85
		Cu	93

$$B_{th}\left[\frac{m^3}{Kg_{vs}}\right] = \frac{a*22.415}{12a+b+16c+14d} \quad (4)$$

$$M_{th}\left[\frac{m^3}{Kg_{vs}}\right] = \frac{\left(\frac{4a+b-2c-3d}{8}\right)*22.415}{12a+b+16c+14d} \quad (5)$$

3. Results and discussion

3.1. DWTS characterization

The composition of DWTS was given in Table 2. The main constituents of DWTS were Fe_2O_3, SiO_2, CaO, and Al_2O_3, respectively. The high amount of Fe_2O_3 identified by X-ray fluorescence (XRF) analysis was due to iron chloride addition as a flocculent in the process of drinking water treatment. The component of SiO_2 was ascribed to suspended solid include of different types of clay. Small quantities of other oxide such as MgO, P_2O_5, MnO, TiO_2, K_2O, and Na_2O were also detected. Besides, some trace elements including Ni, Cr, Co, Zn, Cu, Ba, Sr, Cl, and Zr were detected in ppm levels in DWTS.

3.2. Statistical analysis

The biomethane potential of the positive control was 380 Nml/g VS which is in acceptable range according to the guideline proposed by Holliger et al. (2016). This confirms the suitability of the inoculum as well as the correctness of the methane volume measurement method. The results of ANOVA analysis showed that the effect of DWTS on biogas and methane yield from food waste was significant (Table 3).

Table 3
One-way ANOVA for biogas and methane yields.

	Source of variations	Sum of squares	*df*	Mean square	F	Sig.
Biogas yield	Between groups	146870.585	4	36717.646	44.031	.000
	Within groups	8339.114	10	833.911		
	Total	155209.699	14			
Methane yield	Between groups	73080.242	4	18270.060	31.100	.000
	Within groups	5874.611	10	587.461		
	Total	78954.852	14			

3.3. Effects of DWTS on biogas and methane production

Biogas yield was significantly improved when treated with any concentrations of DWTS (Fig. 1b). The difference between the biogas yield from 6 mg/kg to 12 mg/kg of DWTS was not significant (Fig. 2). In the presence of 12 mg/kg DWTS, about 90% of the total biogas (555 mL.g^{-1} VS) was produced after 6 days of the startup, while it lasted 11 days for the blank digester to produce the same percentage (365 mL.g^{-1} VS). The duration of experiments by adding 6 and 12 mg/kg DWTS was 12 days which was much shorter than the control (Fig. 1c). From economical point of view, shorter hydraulic retention time will allow more daily feeding of the tank, which results in more biogas yield per volume of the digester. This means less capital cost for a given power generation capacity.

Methanogenic activity was clearly stimulated during the startup of the reactors with additive (Fig. 1c and d). Biomethane yield in the presence of DWTS was significantly higher than the blank reactor (Fig. 2). In S_2, S_6, S_{12}, and S_{18} the total methane yield was 1.43, 1.58, 1.57, and 1.41 times the methane produced by the control. Insignificant difference was observed S_6 and S_{12}. Comparing to the control digester, up to 65 and 58 percent increase in biogas and methane yields was observed when 6 mg/kg of DWTS was added to the substrate respectively. The highest methane yield of 522 mL/g VS was observed in S_6. Nevertheless, as mentioned before, adding 18 mg/kg DWTS reduced the biogas and methane yield, which shows getting far beyond the optimal concentration limit. More concentration of DWTS is very likely to show significant inhibitory effect.

Sulfur and phosphorus contain of the food waste were 0.25 and 0.14% respectively (Table 1). These two elements are considered as macro nutrients for methane formation in AD (Deublein and Steinhauser, 2011). From Table 2, the DWTS contains 0.4% P_2O_5 which could be served as macro nutrient for the process. Moreover, the concentration of trace elements (e.g. Fe, Al, K, Mn, Ni, Co, and etc) were much lower than the optimum range recommended by (Deublein and Steinhauser, 2011). From Table 2, it can be seen that all these elements are present in DWTS.

Probably the most effective trace element was Fe as it is the predominant element in the DWTS (almost 40% of Fe_2O_3) (Table 2) and has a stabilizing characteristic in AD of food wastes (Mao et al., 2015). Therefore, one can conclude that DWTS acts as a mixture of different trace elements with synergistic and antagonistic effects, consequent of which, was to enhance the methane production from food wastes. A key factor in the overall economic efficiency of a biogas plant is the volumetric methane yield; the total methane yield per effective volume of the digester. The calculations revealed that the volumetric methane yields were 4.9, 8.3, 8.9, 9.0, and 8.1 m^3 per cubic meter of the digester for the control, 2, 6, 12, and 18 mg/kg DWTS respectively. This is relatively high when compared to literatures such as (Zhang et al., 2015). "Although supplementation of micro-nutrients and trace elements could be a simple way to achieve AD process stabilization and efficient biogas generation, the economic feasibility of trace elements should be dependent on their cost" (Mao et al., 2015). Nevertheless, DWTS is a free of charge mixture of different trace elements with high impact on biomethane yield. It could be the subject for further research in order to be used in large scale biogas plants.

3.4. Kinetic model of biogas production

To evaluate fitness of the modified Gompertz model, the experimental methane data were plotted against the predicted methane data, as presented in Fig. 3. The calculated kinetic constants were listed in Table 4. The maximum volume of the methane S_0, S_2, S_6, S_{12}, and S_{18} was estimated to be 320, 471, 513, 512, 462 mL respectively. The calculated lag times were found to be in between 3.3 and 4.7 days. The obtained R^2 values were higher than 0.994 indicated that the modified Gompertz fitted very well with the experimental values. The findings

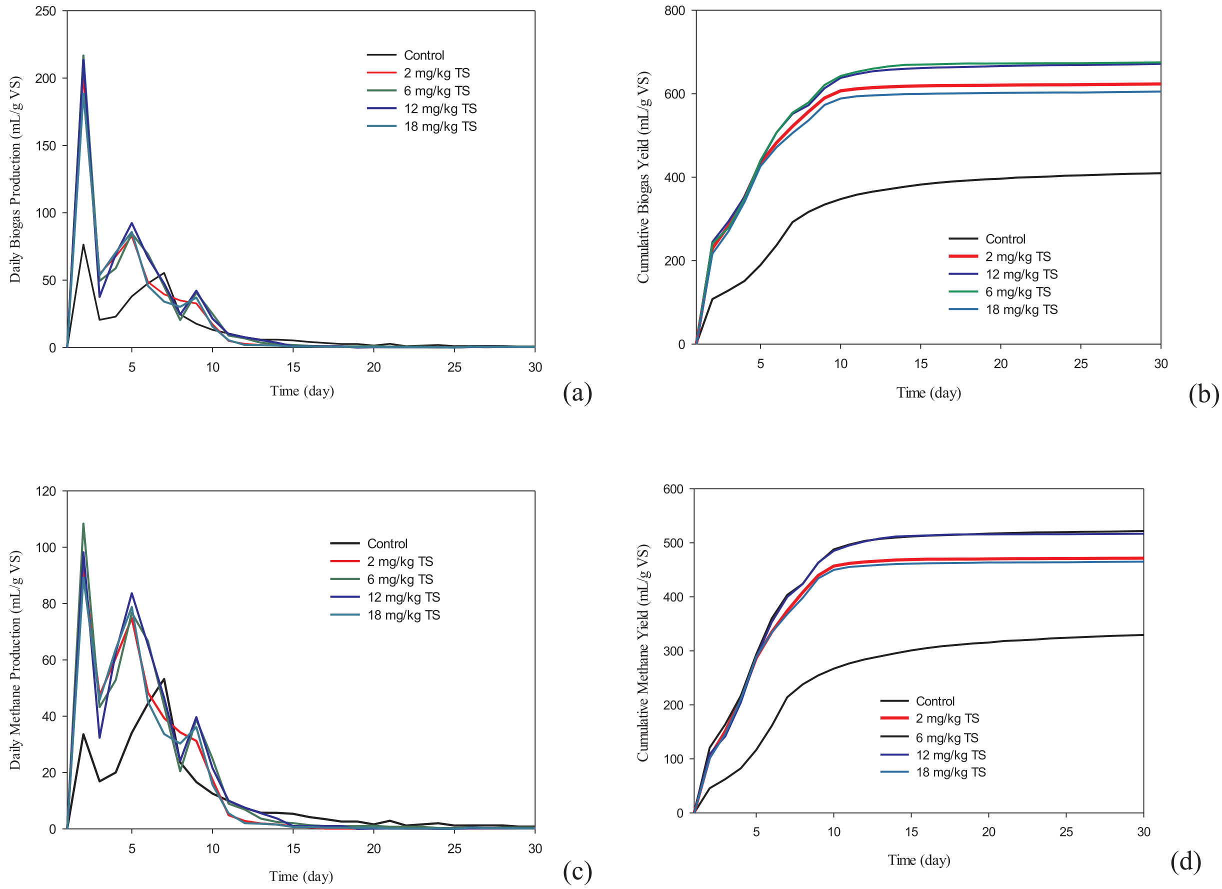

Fig. 1. Effect of DWTS on daily and cumulative biogas (a and b) and methane (c and d) production from food waste.

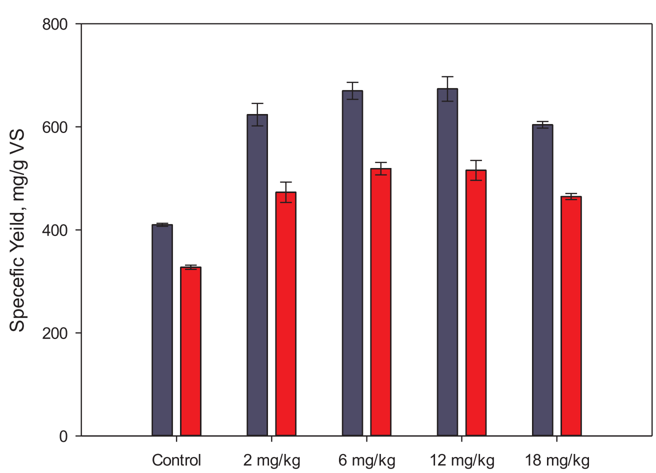

Fig. 2. Comparison of the total biogas and methane production from food waste at different concentrations of DWTS.

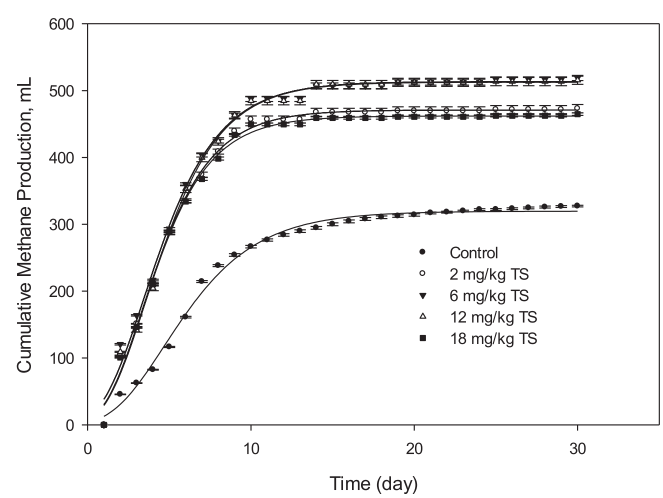

Fig. 3. Comparison of the experimental cumulative biogas yield with the results obtained by modified Gompertz model.

from kinetic study using first-order kinetic model were presented in Table 5. The k for all levels of DWTS were almost the same (from 1.71 to 1.88/day). The minimum k value (0.12/day) was obtained for S_0 sample. The R^2 was calculated to be between 0.948 and 0.953, indicating a relatively well fitness of experimental data in the model. The difference between the predicted methane values and the actual values were lesser in the Competz model (2–7) compared to first order model (13–19). Thus, the modified Gompertz model is a more appropriate in the biogas production from anaerobic bacteria. Similar findings have been reported with the studies evaluated the kinetic model of cumulative biogas production (Kafle and Kim, 2013; Lizama et al., 2017).

3.5. *Theoretical biogas production*

The chemical formula of food waste was determined by elemental analysis. The molar composition of the biogas produced from one mole of food waste is described as follow:

$$C_{17.91}H_{26.13}O_{15.28}N + 4.48H_2O \rightarrow 8.02CH_4 + 9.88CO_2 + NH_3 \quad (6)$$

The estimated biogas and methane production of the food waste were 803 and 360 L/kg VS, respectively. The ratio of the observed biogas production in empirical conditions to the theoretical biogas production (ε) was different in the all experiments. This value was 0.51

Table 4
Results of kinetic study using pseudo first-order model.

Additive concentration (mg kg^{-1})	R^2	k (1/day)		First-order kinetic model			
				Methane yield (L kg^{-1} TS)			
				Calculated		Measured	Difference
		Value	Standard error	Value	Standard error	Value	
0	0.953	0.12	0.0101	346	9.6432	327	19
2	0.949	0.188	0.0136	487	8.6309	473	14
6	0.949	0.186	0.0118	532.4	8.9871	518	14
12	0.950	0.171	0.0126	533.4	10.1794	515	18
18	0.948	0.188	0.0139	477	8.5102	464	13

Table 5
Results of kinetic study using modified Gompertz model.

Additive concentration (mg kg^{-1})	R^2	R_{max} (L Kg^{-1} TS-d)		λ (day)		Modified Gompertz model			
						Methane yield (L kg^{-1} TS)			
						Predicted		Measured	Difference
		Value	Standard error	Value	Standard error	Value	Standard error		
0	0.994	37.303	1.4211	4.7	0.0970	320	2.1471	327	7
2	0.996	73.966	2.3627	3.4	0.0612	471	2.0415	473	2
6	0.994	73.830	2.7163	3.4	0.0764	513	2.7076	518	5
12	0.995	75.262	2.5147	3.6	0.0684	512	2.4530	515	3
18	0.996	73.984	2.3661	3.3	0.0602	462	1.9806	464	2

for control sample was 0.51 while for S_2, S_6, S_{12}, and S_{18} were 0.77, 0.83, 0.84, and 0.75, respectively. It shows that the quantity of the produced biogas in the presence of DWTS are closer to the theoretical biogas. Since the estimation of theoretical biogas production is based on the elemental composition. This analysis does not differentiate between biodegradable and non-biodegradable matter. Therefore, the ε value is smaller than 1, as confirmed by other studies (Klimiuk et al., 2010; Lesteur et al., 2010; Nielfa et al., 2015). The ε value is larger than 1 is possible when co-digestion of certain substrates has a synergistic effect in the final production (Nielfa et al., 2015).

4. Conclusion

Drinking water treatment sludge which contained essential nutrients was used as a mixture cheap additive for biogas production. DWTS showed a significant effect on biomethane production in mesophilic AD of food waste. A maximum methane yield of 522 Nml/g VS was observed by adding 6 mg/kg DWTS. This corresponds to 59% improvement in comparison with the control assay. Moreover, shorter digestion time is needed in the presence of the DWTS. More than 90% of the biogas was produced in the first 6 days of the experiment. The modified Gompertz model was more appropriate for prediction of methane yield when compared to the first order kinetic model.

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