THE EFFECT OF INTERMEDIATE OZONATION PROCESS ON IMPROVING BIOGAS PRODUCTION FROM CO-DIGESTION OF AGRICULTURAL WASTE AND MANURE

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ABSTRACT

Anaerobic co-digestion of agricultural solid waste, wastewater, and manure was evaluated in batch reactor. The performance of anaerobic digestion (AD) was monitored by assessing the methane production potential, maximum methane production rate and methane production lag time. An intermediate advanced oxidation processes by ozone was used to increase in the amount of methane produced and reduce the AD time. The production of methane from pure substrate (cow manure and wheat straw) was found to be 325 and 130 L/kg VS, mixed substrate of wheat straw, cattle manure and wastewater generated more than 368 L/kg VS. An intermediate ozonation process between two AD processes increased the % methane recovery form the ultimate value 60-85%, and reduce the total AD time to 20 days.

Keywords: Agricultural waste, inhibition, manure, methane yield, sludge characteristics, chemical oxidation

1 INTRODUCTION

Millions tons of solid waste (SW) are generated from agricultural, municipal, and industrial sources every year. The amounts of SW are expected to increase exponentially in the coming decades, due to the growth of the world's population and the increase in levels of development (Kanat, 2010). The agricultural solid waste generated in Jordan, a developing country, were estimated to be at 3,464.1 tons in 2009 (Almomani and Shawaqfah., 2013). For developed countries, the per capita amount of SW generated can be as much as 10 orders of magnitude higher than in developing countries. The accumulation of solid waste threatens public health and contributes to environmental pollution. The traditional treatment of agricultural solid waste, including land applications and land filling, have resulted in subsequent environmental problems in the ecosystem (air, soil, and water) (Salihoglu, 2010; Daskalopoulos and Badr, 1997; Debishree and Samadder, 2014) . Incineration is another treatment alternative. However, its low capacity, low energy output, and the emission of polluting gases limit its applicability (Chang et al., 1999; Porteous, 2001; Cheng, and Hu, 2010; Montejo et al., 2011). Therefore, there is a great need for an effective process that can treat such solid waste, reducing their hazardous effects with a minimum impact on the environment.

Anaerobic digestion (AD) of solid waste and animal manure is an effective way to reduce the impact of the waste and to reduce the amounts of greenhouse gas emission (Macias-Corral et al., 2008; Ashekuzzaman and Poulsen, 2011). In addition, AD technology can play an essential rule in reducing the amounts of ammonia and methane emitted from manure storage facilities. Although anaerobic digestion is a very well-known technology, a fundamental gap in knowledge still exists regarding the response of AD and embedded microbial communities to solid waste treatment. Most studies investigating anaerobic processes have considered one type of solid waste, as units that are able to process mixture of waste are rare (Murto et al., 2004). The aim of this study is to investigate and to optimize the performance of AD technology as a means of treatment for agricultural solid waste and to further develop a fundamental understanding of the effect of different operational parameters (total solid content, substrate structure, and volatile solids) on the performance of the AD process and on methane production. Furthermore, the effect of intermediate chemical oxidation and strategies for improving the digestion of different substrates and for enhancing methane production was investigated.

2 MATERIALS AND METHODS

2.1 Experimental set-up

Chlorella vulgaris was used in this study and purchased Batch digestion was used to determine the ultimate methane yield for each substrate. The experiments were carried out in a jacketed 1.0 L reactors, which equipped with mixer, sampling outlet, gas-sampling port, and feed inlet. The methane produced during the AD was collected in a gas collection bags and kept there for further analysis. The reactors were purged prior to operation with nitrogen gas for 10 min to ensure anaerobic conditions. The digestion was performed at 25 ± 1 °C. The content of the reactor was mixed 4 times per day at mixing intensity 80 rpm for 20 min. The experiments were carried out for a period of 96 days to determine the maximum methane that can be generated from each substrate.

2.2 Preparation of microalgae samples

Table 1 shows the substrates characteristics used in the AD experiments. Agricultural waste (Wheat straw), animal manure (Cow and Cattle), wood dust and wastewater were mixed in different portions (see table 1) to produce a substrate with specific solid contents, carbon-to-nitrogen ratio (C/N ratio), ammonia content, volatile fatty acids and chemical oxygen demand. In table 1, C-1, C-2 and S-1 represent pure substrate of cow manure, cattle manure and wheat straw, respectively. AgrMun-i represent mixed substrate prepared by mixing of wheat straw, animal manure (cow or cattle), wood dust and wastewater in different portions. AgrMun-1 was prepared by mixing wheat straw (1 w/w%) cattle manure (35%) and wastewater (64%), AgrMun-2 was prepared by mixing wood dust (30%), cattle manure (30%) and wastewater (40%), AgrMun-3 was prepared by mixing cow manure (12%), cattle manure (12%), wastewater (66%) and wood dust (10%), AgrMun-4 was prepared by mixing wheat straw (10%), cattle manure (10%) and wastewater (80 %), and AgrMun-5 was prepared by mixing wood dust (10%), cattle manure (15%) and wastewater (75%).The substrates were prepared and immediately stored in a refrigerator at approximately 4 $^{\circ}$C.

Table 1: Main characteristics of the substrates used in the AD experiments

	C-1	C-2	S-1	AgrMun-1	AgrMun-2	AgrMun-3	AgrMun-4	AgrMun-5
Total solids (g/kg)	144	138	910	910	42	58	68	104
Volatile solids (% of TS)	66	66	88	76	66	78	73	68
Ash (% FM basis)	1.1	1.21	4.1	1.56	1.45	1.34	1.2	1.2
pH	7.2	6.86	ND	7.1	7.4	7.1	7.5	7.4
C/N	19	21	87	32	26	35	28	28
Carbon content	18.5 [a]	19.9[a]	39[a]	220[b]	290	340 [b]	185[b]	195[b]
TN	0.99 [c]	1.01[c]	0.45[c]	35[d]	32 [d]	26 [d]	20 [d]	16 [d]
Acetate (g/kg)	ND	ND	ND	1.4	ND	0.6	0.58	0.62
Propionate (g/kg)	ND	ND	ND	0.55	ND	0.33	0.31	0.33
Butyrate (g/kg)	ND	ND	ND	0.21	ND	0.12	0.12	0.13

2.3 Analytical methods

The volume of gas produced in AD was measured using two graduated cylinders. Initially, the first cylinder was filled with water and the second was inverted. The inverted cylinder was connected from the top via rubber tubes to the biogas bag. Sliding the upper cylinder upward creates a vacuum between the water surface and the upper cylinder cover that pulls biogas from the bag. When all the biogas was pulled out of the bag, the volume of the gas was recorded. The cylinders were then disconnected from the AD system and connected to gas chromatography (GC), with which the gas composition was analyzed. A control experiment was performed to correct the loss of CO_2 due to solubilization in water under the experiment conditions.

Ammonia was measured according to Standard Method 4500–NH_3 B and C,(APHA, 1995) using a HACH spectrophotometer at 425 nm (DR2000 HACH, CO, USA). The total solids (TS) and volatile solids (VS) measurements of the substrate were measured in duplicate and are reported as average values of the duplicate measurements. TS and TVS were determined by weighing the dried solids (105 °C) and igniting them at 550 °C for 15 minutes. TS and VS measurements were carried out following Standard Methods (APHA, 1995) 2540 D and E. The sludge filtration index (SFI) and the sludge volume index (SVI) were measured according to the procedure proposed by Al Momani et al., 2010 and Almomani et al., 2011.

The organic content of the substrates was determined by measuring the total organic carbon using a TOC analyzer (TOC 5000, Shimadzu Co., Ltd.).

The Total nitrogen (TN) in the water samples was measured using a Shimadzu TOC-VCPH analyzer. Measurements were carried out in triplicate and reported as an average value at 95% confidence intervals. The detection limit of the TN analyzer was determined to be in the range of ± 0.1 mg.N.L^{-1} using standard solution.

Chemical oxygen demand tests (COD) were carried out using HACH COD reagents according to the Standard Methods(APHA 1995), Method 5220D.

2.4 Experimental procedure

The procedure used to determine the ultimate methane yield include pre-incubation of inoculum for 10 days at 25 $^{\circ}$C in order to deplete the residual biodegradable organic material. The composition of the inoculum used in this test consist of 4.5 % of dry matter (DM), 1.2 % of ash content, 3.1 % of volatile solids (VS),1.23 g total ammonia and as a maximum 0.15g.L^{-1} volatile fatty acids (VFA). The test was performed at pH of 8.00. For each substrate six reactors with a total volume of 1 L were used. The first three bottles were filled with a mixture of substrate inoculum with a ratio of approx. 1:0.25, determined on VS basis. The other three bottles were filled only with inoculum and used as blanks. The reactors were then sealed and the headspace was flushed with pure N_2 for 5 min. The bottles were incubated after that at 25±1 $^{\circ}$C for 96 days. The cumulative methane volume produced from each substrate was corrected by subtraction the volume of methane produced in blank bottles.

Two-stages digestion with an intermediate chemical oxidation was performed by digestion of the substrate from table 1 in AD for 15 days (first stage of digestion). After that, the substrate was then oxidized with ozone at different specific inlet ozone concentration (1, 3, and 5 mg/L) and a specific gas flow rate of 25 L/h for 10 min. Ozonation experiments were carried out using an ozone generator (Anseros, Ozone generator COM-AD-01). Ozone was produced onsite from ultrapure O_2. Inlet ozone pumped to the substrate was measured by an inlet ozone analyzer (Ozomat GM-60000-OEM). Afterwards, the substrate was diverted to AD for the second stage of digestion for another 15 days. The cumulative methane produced from the two digestion processes was reported as total cumulative methane production.

3. RESULTS AND DISCUSSION

Fig. 1(a) and (b) show the cumulative methane production and methane production rate for batch experiments carried out with pure substrate and mixed subtract for 96 days. The compositions and characteristics of the substrate used in these experiments were presented in table 1. Mixed substrate produced more methane than pure substrate. Pure cow manure and wheat straw produced ultimate methane yield of 325 and 130 L/kg VS, respectively. On the other hand, the mixed substrate (e.g. ArgMun-2) which consist of wheat straw, cattle manure and wastewater generated more than 368 L/kg VS during the same digestion period. The reason behind, the differences in methane production and methane production rate can be due to the differences in the chemical composition of each substrate

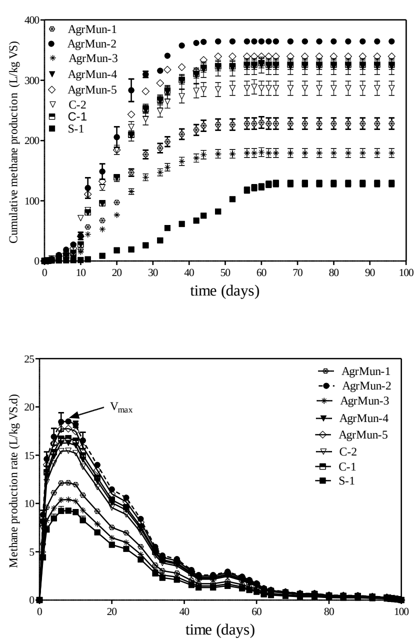

Figure 1: (a) Cumulative methane production and (b) methane production rate during batch experiments for pure and mixed substrates.

An intermediate ozonation step was introduced to measure the effect of inter-stage chemical oxidation on the methane yield and the reduction of AD digestion time. The substrates used in this set of experiments are (AgMun1, 2, 3, 4and C-2). Experiments were carried out by digesting these substrates in AD for 10 days; after that, the substrate was oxidized with ozone for 10 min with different inlet ozone doses (1, 3, and 5 mg/L). Following this, the substrate was digested again for another 10 days. Table 2 shows the cumulative methane production, maximum methane production rate, and the % methane recovery from ultimate methane yield for the experiments carried out with two stages of anaerobic digestion and an intermediate chemical oxidation stage by ozone.

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Table 4: Cumulative methane production, maximum methane production rate and % methane recovery from ultimate methane yield for two stages anaerobic digestion and an intermediate chemical oxidation (ozone)

	Inlet Ozone dose (mg/L)	Cumulative Methane (L/kg VS),	Maximum methane production rate (MPR_{max}) (L/kg VS d)	% methane recovery from ultimate methane yield
AgrMun-1	1	190	7	83.0
	3	195	7.5	85.2
	5	201	7.9	87.8
AgrMun-2	1	300	16	81.5
	3	309	16.7	84.0
	5	316	16.9	85.9
AgrMun-3	1	120	5.5	66.7
	3	125	5.9	69.4
	5	130	6.1	72.2
AgrMun-4	1	265	13.2	80.8
	3	269	13.6	82.0
	5	273	14.1	83.2
C-2	1	181	12.1	63.3
	3	193	12.6	67.5
	5	197	13.0	68.9

Using ozone to oxidize the sludge produced from the first digestion increases the methane that can be produced from these substrates and reduce the total time of digestion to 20 days. The % methane recovery from the ultimate methane value ranged from 63.3%–68.9 %, 81%–85% 66.7%-72.2%, 80%–83.2% and 83% -87.8% for AgrMun-1, 2, 3, 4, C-2, AgrMun-1 and 5, respectively. The percent ozone used (% ∇) in oxidizing the sludge was calculated by Equation (1). The equation assumes that the concentration of ozone in the reactor is negligible.

$$\nabla = \frac{\{Q_{Gas} * ([O_3]_{gas,in} - [O_3]_{gas,out})\Delta t\}}{V_{Reactor}} \qquad (1)$$

Here, Q_{gas} is the gas flow rate to the reactor, $[O_3]_{gas,\ in}$ is the concentration of ozone in the inlet gas, $[O_3]_{gas,\ out}$ is the concentration of ozone in the outlet gas. For the

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experiments carried out with inlet ozone concentrations of 1 and 3 mg/L, the residual ozone in the gas was found to be zero, indicating that all the ozone was used in sludge oxidation. However, the experiment carried out with an inlet concentration of 5 mg/L showed very small ozone residuals (% ∇ ~ 89%–92%). Table 2 also shows that the difference in methane production between the sludge treated with 3 mg/L and 5 mg/L is no more than 5%. Accordingly, a chemical oxidation step with an initial ozone concentration of 3 mg/L is recommended.

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Conclusion:

This study showed that Methane production from mixed substrate is higher than pure substrate. Pure cow manure and wheat straw produced ultimate methane yield of 325 and 130 L/kg VS, while mixed substrate of wheat straw, cattle manure and wastewater generated more than 368 L/kg VS during 96 days digestion period. An intermediate oxidation process between two AD stages can be used to improve the methane production and to reduce the production of sludge from agriculture solid waste digestion. Using ozone to oxidize the sludge produced from the first digestion increases the methane that can be produced from these substrates and reduce the total time of digestion to 20 days. The % methane recovery from the ultimate methane value ranged from 63.3%–68.9 %, 81%–85% 66.7%-72.2%, 80%–83.2% and 83% -87.8%.

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