The role of metals in methane production from shredder waste in landfills

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Abstract

In this study, different types of shredder waste (i.e. fresh and old samples) were characterized. The role of metals in methane (CH_4) production from shredder waste was assessed. Shredder waste and sterilized shredder waste were incubated at 37 ºC and moisture content of 75 % w/w, and inoculum addition of 30 % of the samples wet weight. Moreover, the ability of metals (iron, aluminum, zinc and copper) contained in shredder waste to produce H_2 was investigated.

Iron, aluminum and zinc produced H_2 in contact with water under anaerobic condition, and the produced H_2 was utilized in biological experiments by hydrogenotrophic methanogens to convert CO_2 to CH_4. Addition of aluminum and zinc to shredder waste resulted in higher CH_4 production while adding iron and copper to shredder waste resulted in inhibition of CH_4 production. This suggested that aluminum and zinc contribute to high CH_4 production from shredder waste by providing H_2 for hydrogenotrophic methanogens. Gas compositions with higher CH_4 and lower CO_2 observed in landfilled shredder waste are thus most likely due to the consumption of existing CO_2 in the produced biogas and the produced H_2 by biocorrosion of aluminum and zinc by methanogens.

Keywords

Anaerobic digestion, biocorrosion, elemental metals, anaerobic batch incubation.

1. Introduction

Shredder waste (SW) is the waste produced after mechanical treatment of iron and metal containing wastes including vehicles, bicycles, and white goods. SW consists of mainly plastic, metals, rubber, textile, foam, glass and wood. Significant production of landfill gas has been observed at SW monofills [1, 2]. This is surprising as SW usually contains low fractions of biodegradable waste and the biodegradable fractions have a high content of lignocellulosic components such as wood and cardboard. The reason for high landfill gas production from SW is unknown. Moreover, previous studies have shown gas compositions in SW, which differed from conventional landfill gas—a high CH_4 content and very low or no CO_2 [2, 3]. The reason for the unusual gas composition is also unknown.

Although SW has passed through metal-separation technologies, it still contains metals. We hypothesized that high CH_4 production from SW and unusual gas composition could be due to H_2 production by biocorrosion of metals in the waste, supporting hydrogenotrophic methanogens to convert CO_2 to CH_4, resulting in higher CH_4 content and lower CO_2. The objective of this study was to investigate the role of metals contained in SW in CH_4 production from SW.

2. Material and methods

2.1. Waste sampling, sample preparation and characterization

SW samples were collected from Odense Nord landfill located in Funen, Denmark. SW samples were taken according to the year of deposition: 2009 (SW2009) and 2012 (SW2012). Fresh samples of SW (year 2015) were obtained by sampling the waste on the same day as it was deposited in the waste cell. Samples were taken with an excavator or wheel loader, laid out in a long pile at the landfill, and subdivided three times using the long pile-alternate shovel method.

Fifty kg of each SW sample was transported to the laboratory and kept at 10 °C. In the laboratory, the samples were subdivided three times using the long pile-alternate shovel method, resulting in 5-7 kg of subsamples. Fresh SW (FSW) samples and samples from 2009 and 2012 were mixed together based on equal wet weight to make one composite sample (COM), representative of the whole landfill. Five kg of each sample was dried at 105 ºC for 24 hours and total solids (TS) were calculated based on the difference in the weight of the sample before and after drying.

Metals, wires and stones were separated manually from the dried samples. The resulting samples (of about 3-4 kg) were size reduced using a cutter mill with 1 mm sieve. The outcome of the cutter mill was analyzed for volatile solids (VS), total carbon (TC), and total organic carbon (TOC). TS and VS were measured according to APHA Standard Methods. TC and TOC were analyzed using a LECO Induction Furnace CS-200 oven on approximately 0.1 g of dried sample ground to 1 mm according to EN 13137, 2001. All measurements were done in triplicate.

2.2. Biocorrosion experiment

Biocorrosion incubation experiments were conducted to investigate the hypothesis of CH_4 yield enhancement by H_2 production from biocorrosion of metals. According to the conducted literature review iron (Fe), aluminum (Al), zinc (Zn) and copper (Cu) are the main metals in SW [4-6] and thus were examined for their ability to produce H_2. The experiment had two steps and both were carried out in duplicate in 1 L glass bottles for 20 days in a 37 ºC incubator.

In the first step, H_2 production from elemental metals in contact with water was investigated. In this step, 2.5 g of elemental metals was placed in each incubation bottle and 250 mL of tap water was added to each. In step two, the CH_4 production enhancement of inoculum by addition of metals was investigated. In this step, incubation bottles contained 2.5 g of elemental metals and 250 g of inoculum, resulting a concentration of 10 g/L of liquid for each metal. Bottles containing only inoculum were used as blank to calculate CH_4 production from inoculum alone. Bottles were flushed with N_2 for 15 minutes to establish an anaerobic condition, and then sealed with rubber septum.

Gas volumes were converted to STP conditions. Gas samples (0.3 mL) were taken from the headspace of the bottles and directly injected to a thermo-scientific trace gas chromatograph (TRACE 1310 GC, Molsieve, 0.53 mm, 30 m) with a thermal conductivity detector (TCD). Mesophilic inoculum, used in this experiment, was collected from a biogas plant located at Va Syd Sjölunda wastewater treatment plant (WWTP), Malmo, Sweden. Powders of elemental metals were obtained from Sigma-Aldrich.

2.3. Batch incubation experiment

Batch incubation experiments were performed in glass bottles with total volumes of 5 L at 37 °C. All bottles were connected to 2 L aluminum gas bags by a PVC tube to collect the produced biogas. All PVC tubes were equipped with a rubber septum for sampling the produced biogas. At each measurement of gas composition, 5 mL gas samples were taken from the rubber septum with a syringe and injected immediately into evacuated glass vials equipped with rubber septa (Exetainer Vail, Labco Ltd, Lampeter, UK), which then were analyzed by a gas chromatograph (490-PRO Micro GC).

In order to investigate the role of metals on the CH_4 production, Fe, Al, Zn, and Cu with dimension of 5 mm × 5 mm and concentrations of 5, 2, 2, and 2 % of the substrate wet weight (25, 10, 10, 10 g/L of liquid), respectively, were added separately to the incubation bottles containing the COM samples. Moisture content of the samples was adjusted to 75 % w/w, and inoculum (30 % of substrate wet weight) was added to the incubation bottles. One bottle containing only inoculum and water were used as blank to determine CH_4 production from the inoculum alone, which was subtracted from the CH_4 production of waste samples. Mesophilic inoculum collected from the biogas plant located at Va Syd Sjölunda WWTP (Malmo, Sweden) was used in this experiment.

Abiotic control experiments were also performed by sterilizing samples (autoclaving three times for 1 h at 121 ºC) to measure possible CH_4 production due to non-microbial processes. All reactors were flushed for 20 minutes with nitrogen gas to make an anaerobic condition. The biogas volume was measured using a water displacement method. Gas volumes were converted to STP conditions. CH_4 and CO_2 concentrations were measured by a 490-PRO Micro GC (Agilent Technologies Denmark Aps, Glostrup, Denmark) with a TCD.

3. Results and discussion

3.1. Waste characterization

Table 1 shows waste characterization in terms of TS, VS, TC, TOC. Overall, low variation was observed in the TS content of different waste samples. FSW had the highest TS content (91 %), while COM had the lowest (82 %). TC contents of waste samples were from 14 to 24 % with FSW having the highest (24 %) and SW2009 the lowest (14 %). The TS and TC content of the waste samples were comparable to previous studies [7-10].

FSW contained the highest amount of VS, and TOC (32 % and 21 %, respectively), which is reasonable as this sample was fresh and thus had not undergone anaerobic degradation in the landfill. The COM sample was a mix of FSW, SW2012 and SW2009 and it had VS and TOC contents between these substrates. SW2012 and SW2009 had lower VS and TOC contents than FSW, most likely as a result of anaerobic degradation since their deposition in the landfill.

Table 1. Characteristics of different fractions of SW. Numbers in brackets give the standard deviation.

Shredder waste	TS (%, kg/kg wet waste)	VS (%, kg/kg wet waste)	TC (%, kg/kg dry waste)	TOC (%, kg/kg dry waste)
SW deposited in 2009 (SW2009)	89 (6.54)	18 (1.17)	14 (0.67)	11 (0.93)
SW deposited in 2012 (SW2012)	83 (1.48)	20 (0.35)	15 (0.82)	14 (0.57)
Fresh sample (FSW)	91 (0.02)	32 (1.15)	24 (1.99)	21 (1.29)
Composite SW sample (COM) [a]	82 (0.71)	24 (0.92)	18 (1.24)	16 (0.60)

[a] *Mix of SW2009, SW2012 and FSW.*

3.2. Biocorrosion experiment

Fig. 1 presents the cumulative H_2 (1a) and CH_4 production curves (1b) over a 20-day incubation period. As can be seen from Fig. 1a, Fe in water (Water+Fe incubation) showed the highest H_2 generation, followed by Al and Zn in water, respectively. H_2 was not generated by Cu in water. Accumulation of H_2 was not observed in biological (containing inoculum) incubations (Fig. 1a). This was expected, as hydrogenotrophic methanogenesis is a very fast process, meaning that the generated H_2 is consumed rapidly in the production of CH_4. This helps to keep the H_2 pressure low, which is needed for successful anaerobic digestion processes to occur.

Fig. 1b shows that adding Fe, Al and Zn to inoculum resulted in higher CH_4 generation than inoculum alone. However, addition of Cu to inoculum (Inoc+Cu incubation) resulted in lower CH_4 generation compared to inoculum alone. These results indicate that H_2 generation from corrosion of Fe, Al, and Zn can be utilized by hydrogenotrophic methanogens to convert CO_2 to CH_4. CH_4 generation was not observed in incubations containing water and metals, indicating there was no chemical production of CH_4.

The results of this experiment were in line with previous studies. For instance, Belay and Daniels [11], Hu et al. [12] and Lorowitz et al. [13] observed improvement of CH_4 production from certain types of methanogenic cultures and waste activated sludge by addition of Fe, Al and Zn due to H_2 production by these metals. Inhibition of CH_4 production by addition of Cu was also observed in previous studies [11, 14, 15].

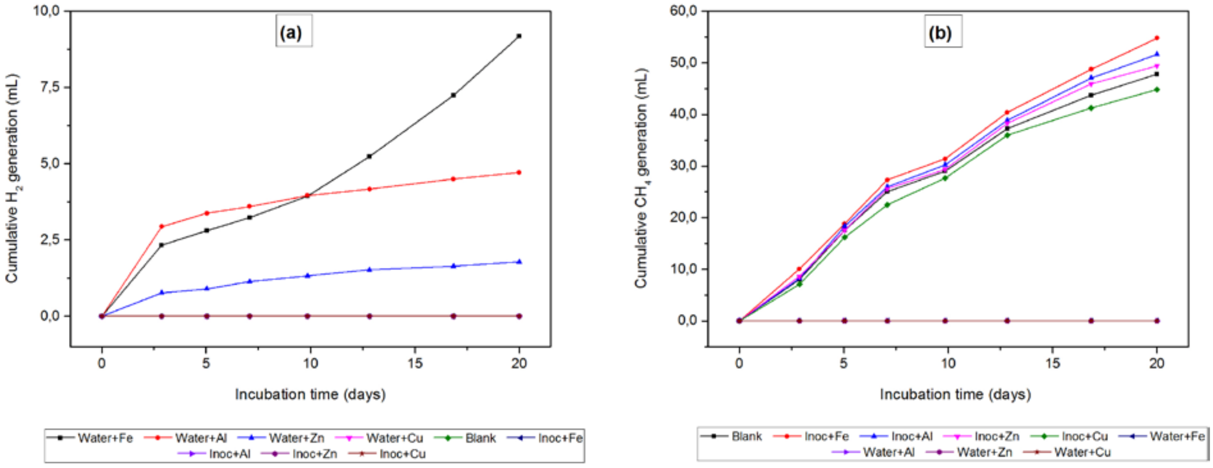

Fig 1. Cumulative H_2 (a) and CH_4 production curves (b) in biocorrosion experiment over period of 20 days. Please note that the H_2 production from Water+Cu, Blank, Inoc+Fe, Inoc+Al, Inoc+Zn, Inoc+Cu incubations (Fig. 1a), and the CH_4 production from Water+Fe, Water+Al, Water+Zn and Water+Cu incubations (Fig. 1b) were all zero and thus the curves are on top of each other and not visible on the graph.

3.3. Batch incubation experiment

Fig. 2 shows cumulative CH_4 production curves of all waste samples during 148 days incubation period. Sterilized reactors did not produce CH_4, indicating there was no abiotic production of CH_4 from SW.

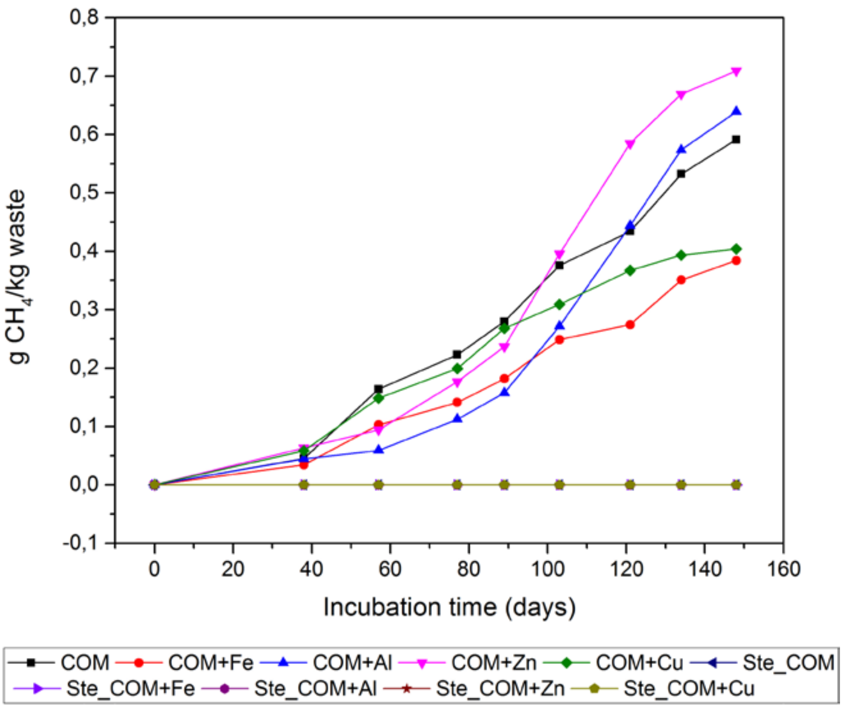

Fig 2. Cumulative CH_4 generation from SW samples, biotic and abiotic experiments, during period of 148 days. Please note that CH_4 production from sterilized reactors (starting with "Ste") were all zero and thus the curves are on top of each other and not visible on the graph.

Addition of Zn and Al to the COM sample resulted in higher CH_4 production in comparison to the experiment with COM alone, while adding Fe and Cu resulted in lower CH_4 production. The obtained results for the impact of Al, Zn and Cu on CH_4 production is in line with the biocorrosion experiment. However, adding Fe resulted in lower CH_4 production in this experiment, while it enhanced CH_4 production in the biocorrosion experiment. This could be due to a higher concentration of Fe in this experiment (25 g/L) compared to the biocorrosion experiment (10 g/L).

Iron (Fe^0 and Fe^{2+}) is an essential microelement for enzymatic reaction and can enhance anaerobic digestion by activating enzymes or H_2 production, or reducing sulfide toxicity [16-18]. However, at high concentrations it can have an inhibitory impact on microorganisms and on the anaerobic digestion process [19, 20].

Table 2 shows the headspace CH_4 and CO_2 concentrations of the biotic reactors measured on the last day of the experiment. The CH_4/CO_2 ratio in the reactors was significantly different compared to the CH_4/CO_2 ratio of conventional landfill gas. Unusual gas composition from SW (high CH_4 and low CO_2 content) has also been reported in previous studies [2, 3]. When comparing the headspace CO_2 concentrations of COM reactor with COM+Al and COM+Zn reactors, it can be seen that COM+Al and COM+Zn reactors have lower headspace CO_2 concentrations. This could be due to utilization of produced H_2 by corrosion of Al and Zn and existing CO_2 in produced biogas by methanogens, resulting in higher CH_4 and lower CO_2 in the headspace of these reactors.

Table 2. CH_4 and CO_2 concentrations in the headspace of the biotic reactors measured on the last day of the experiment (day 148).

Reactor name	CH_4 (%)	CO_2 (%)	CH_4/CO_2
COM	50.4	4.0	12.6
COM+Fe	44.5	3.6	12.4
COM+Al	53.3	3.2	16.5
COM+Zn	52.9	1.7	30.7
COM+Cu	44.7	3.8	11.7

4. Conclusions

Different types of SW were characterized in this study and the role of metals in CH_4 production from them was investigated by performing anaerobic batch incubations. It was evident from the incubation experiments that CH_4 production from SW was not abiotic. Al and Zn were found to produce H_2, and it was observed that the produced H_2 can be consumed by methanogens to convert CO_2 to CH_4. Moreover, results of the incubation experiments indicated that the unusual gas composition (higher CH_4 and lower CO_2), and the relatively high CH_4 production rate from landfilling of SW is most likely due to the consumption of existing CO_2 in the produced biogas and H_2 produced by biocorrosion of Al and Zn by methanogens.

Acknowledgments

The authors would like to thank Hector Garcia and Hector Diaz for their technical support throughout the laboratory experiment. We would also like to thank Rasmus Olsen and Ulrik Lønkjær (Odense Nord Miljøcenter) and Max Granqvist (Va Syd, Sjölunda WWTP) for their help during sample collection. This project was partially financed by Odense Renovation A/S company.

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