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Effect of trace element addition and increasing organic loading rates on the anaerobic digestion of cattle slaughterhouse wastewater

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A B S T R A C T

In this study, anaerobic digestion of slaughterhouse wastewater with the addition of trace elements was monitored for biogas quantity, quality and process stability using CSTR digesters operated at mesophilic temperature. The determination of trace element concentrations was shown to be deficient in Fe, Ni, Co, Mn and Mo compared to recommendations given in the literature. Addition of these trace elements resulted in enhanced degradation efficiency, higher biogas production and improved process stability. Higher organic loading rates and lower hydraulic retention times were achieved in comparison to the control digesters. A critical accumulation of volatile fatty acids was observed at an organic loading rate of $1.82\,g\,L^{-1}\,d^{-1}$ in the control compared to $2.36\,g\,L^{-1}\,d^{-1}$ in the digesters with trace element addition. The improved process stability was evident in the final weeks of experimentation, in which control reactors produced 84% less biogas per day compared to the reactors containing trace elements.

1. Introduction

The Australian red meat processing (RMP) industry has a high energy and water demand and generates significant amounts of liquid and solid wastes (Jensen et al., 2014). Consequently, the industry is increasingly using anaerobic digestion (AD) technology for methane recovery and to reduce the organic loading of wastewaters prior to discharge (McCabe et al., 2014). Some processors in Australia use covered anaerobic lagoons as a secondary wastewater treatment after upstream screening and reduction of fat, oil, and grease (FOG) levels by dissolved air flotation (Harris & McCabe, 2015).

The high organic strength of Australian RMP wastewater can be difficult to degrade by anaerobic digestion due to the relatively high concentrations of lipids and proteins (Johns, 1995). This can cause various problems such as foaming, formation of floating layers and crusts, reaction with cover materials to compromise the material integrity, reduction of the active lagoon volume, clogging of pipes, reducing functionality and service life of sensor technology, wash out of microbial biomass, as well as inhibiting the process by long chain fatty acids, ammonia, and hydrogen-sulphide (Chen et al., 2008; Harris & McCabe, 2015; Long et al., 2012; Schmidt et al., 2018).

Different measures of improving FOG degradation and the reduction of subsequent negative effects have been investigated in various studies, ranging from different digestion technologies to operational parameters such as temperature and stirring and different pre-treatment options (Harris & McCabe, 2015; Harris et al., 2017; Leon-Becerril et al., 2016; McCabe et al., 2017; Núñez & Martínez, 1999; Picavet & Alves, 2013; Reimann et al., 2005).

One of the parameters that can positively influence the anaerobic process is the addition of trace elements (TE) such as Fe, Ni, Co, and others, that are otherwise deficient in the substrate (Demirel & Scherer, 2011). These TE are an essential part of enzymes and co-factors involved in methanogenesis and therefore can directly affect microbial activity and consequently the resulting degradation efficiency and process stability in an AD system (Thanh et al., 2016). According to Scherer et al. (1983), different species of methanogens can have different requirements with respect to TE concentrations. For example, a positive effect of TE addition on process stability and volatile fatty acid (VFA) degradation was reported for the treatment of solid meat processing wastes (Ortner et al., 2014, 2015). Reducing VFA accumulations allows higher organic loading rate (OLR) and shorter hydraulic retention time (HRT) and therefore a more efficient utilisation of anaerobic digestion technology and auxiliary biogas equipment (Bayr et al., 2012; Schmidt et al., 2013).

There has been no studies which report the effects of TE addition to Australian RMP wastewater and the potential impact on the anaerobic digestion of this high organic strength wastewater. This work reports on the influence of TE addition on AD performance of RMP wastewater during increase of the OLR. The results focus on the effect on biogas quantity, quality, process stability and FOG degradability.

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Table 1
OLR and HRT in the digesters.

Time (d)	OLR ($g\,COD\,L^{-1}\,d^{-1}$)	HRT (d)	Time (d)	OLR ($g\,COD\,L^{-1}\,d^{-1}$)	HRT (d)
0–49	0.41	11.1	129–131	1.49	3.7
50–51	0.31	11.1	132–138	1.66	3.3
52–62	0.46	11.1	139–144	1.82	3
63–69	0.51	10	145	1.88	3
70–76	0.56	9.1	146–147	1.88	3.7
77–83	0.61	8.3	148–153	2.08	3.3
84–89	0.65	6.7	154–155	2.19	3
90–96	0.78	5.6	156–159	2.19	2.6
97–103	0.91	4.8	160–165	2.36	2.4
104–110	1.08	4.8	166	2.53	2.4
111–117	1.23	4.2	167–168	2.53	2.2
118–122	1.38	3.7	169	2.6	2.2
123–124	1.38	3.1	170–172	2.6	2.1
125–128	1.5	2.9	173–176	2.76	2

2. Materials and methods

2.1. Experimental setup

Semi-continuous digestion tests were conducted in a BioReactor Simulator (BRS) system from Bioprocess Control (Lund, Sweden). The BRS system consists of six 2 L continuous stirred tank reactor (CSTR) digesters, a water bath for temperature control (38 °C), and a unit to measure the produced biogas volumes. Volumetric biogas measurement was normalised to 0 °C, 1 atm and corrected for water vapour intern, and is reported as normal millilitres (ml_N). Stirring was paused for about 30 min prior to and during daily substrate addition to allow microbial biomass settling and to reduce washout. Wastewater was collected from a site which operates a covered anaerobic lagoon for methane generation (Oakey Beef Exports, Queensland, Australia). Samples were taken from the influent, which is a mixture of red and green stream after dissolved air flotation (DAF) treatment to recover fat for rendering. More detailed information on lagoon operation and waste stream composition was published by Schmidt et al. (2018).

The OLR was increased step-wise as shown in Table 1, which also shows corresponding decrease in HRT over the 170 day incubation period. From day 51 onwards TE were added to three digesters (labelled TE digesters) and the remaining three were used as controls. Trace element solution consisting of iron (III) chloride, nickel (II) chloride hexahydrate, cobalt (II) chloride hexahydrate, manganese (II) chloride tetrahydrate and ammonium molybdate tetrahydrate was added during daily substrate addition. The dosage of TE was 1000, 16, 1.8, 300 and 4 $mg\,kg^{-1}$ of total solids in the substrate for Fe, Ni, Co, Mn, and Mo respectively. Operation of the control digesters was stopped on day 150 after process failure (see Section 3.3).

2.2. Analytical methods

Wastewater samples were analysed for total organic carbon, total nitrogen and trace elements (Co, Mn, Mo, Ni, Se, Zn, Fe, W) by an external laboratory (ALS, QLD, Brisbane). Total solids and volatile solids were determined by standard methods (Strach, 2016). Total chemical oxygen demand (COD), VFA, and ammonium-nitrogen (NH_4) in the substrate and effluents were analysed by Merck test kits and a Spectroquant Pharo 100 spectrophotometer. FOG content was measured by InfraCal II (Wilks, USA) after extraction with hexane. Alkalinity and VFA in the effluent was analysed by a two point titration with a TitraLab® AT1000 (Hach). Biogas composition (CH_4, CO_2, O_2, H_2S) was measured by connecting a biogas analyser (Biogas5000, Geotechnical Instruments, UK) to the individual digesters. Biogas composition was corrected for $CH_4 + CO_2 + O_2 + H_2S = 100\%$ to balance the influence of nitrogen from the air inside the tubing used to connect the gas analyser and the water vapour in the digester headspace. Error bars in the figures represent one standard deviation from the mean.

Table 2
Substrate characteristics (n = 10).

	TS (%FM*)	VS (%TS)	COD ($mg\,L^{-1}$)	FOG ($mg\,L^{-1}$)
min	0.22	62.53	3400	262
max	0.38	78.15	6945	829
Average	0.31 ± 0.05	70.24 ± 4.53	5031 ± 1048	615 ± 196

* FM = fresh matter.

3. Results and discussion

3.1. Wastewater characterisation and trace element concentrations

Table 2 shows the contents of total solids (TS) and volatile solids (VS) and the concentrations of COD and FOG in the wastewater.

These values are comparable with data from literature and represent typical wastewater composition generated by the Australian RMP industry (Jensen et al., 2014). The variation in values are caused by changes in processing, e.g. low FOG value of 262 $mg\,L^{-1}$ was measured shortly after the end of a shut-down period where no cattle were slaughtered for a 3 week period.

The elemental composition of wastewater is given in Table 3. When compared to values recommended in the literature, the trace elements Ni and Mn were below the recommended values, and Fe, Co and Mo were in the lower range. The ratio of carbon to nitrogen (C:N-ratio) in RMP wastewater was found to be 2.7:1 which is very low compared to the recommended value of 40:1 (Weiland, 2010). This is primarily due to the relatively high proportion of proteins compared to other industrial wastewaters and the resulting high nitrogen concentration. This could theoretically lead to ammonia inhibition, however, it is unlikely in this case due to the high water content (> 99%) in the wastewater and the resulting low absolute concentrations of toxic ammonia.

3.2. Biogas quantity and quality

Biogas production was influenced by a number of factors, namely: the variable composition of the input substrate; the increase in OLR and the corresponding decrease of the HRT, resulting in reduced time for degradation; and by the addition of TE. The specific daily biogas production in ml_N per gram of COD added and $ml_N\,g^{-1}$ of VS added is shown in Fig. 1. The biogas production reached values of up to 932 $ml_N\,g_{VS}^{-1}$ and 425 $ml_N\,g_{COD}^{-1}$, with average values of 816 $ml_N\,g_{VS}^{-1}$ and 331 $ml_N\,g_{COD}^{-1}$ under stable process conditions. These values are reflective for a mixture of carbohydrates, proteins and lipids considering the theoretical biogas potential of 750, 800 and 1390 $ml_N\,g_{VS}^{-1}$ for these

Table 3
Trace element composition of the wastewater and recommendations for an optimal range of nutrient and trace element concentrations ($n = 3$).

Parameter	RMP Wastewater ($mg\,kg_{TS}^{-1}$ ± Std.Dev.)	Optimal concentrations[1] ($mg\,kg_{TS}^{-1}$)
Iron	1458 ± 140	750–5000
Nickel	2.40 ± 0.33	4–30
Cobalt	0.61 ± 0.14	0.4–10
Manganese	90.91 ± 2.44	100–1500
Molybdenum	1.49 ± 0.20	0.05–16
Zinc	159.44 ± 17.6	30–400
Tungsten	< detection limit of 0.001 $mg\,L^{-1}$	0.1–30
Selenium	< detection limit of 0.01 $mg\,L^{-1}$	0.05–4

[1] Lemmer et al. (2008).