Mitigation of nitrogen losses with Australian zeolites during the anaerobic digestion of swine manure

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Abstract

Anaerobic digestion (AD) is one of the most effective and sustainable methods of handling swine manure that convert organic wastes into a greener energy, effectively reducing methane (CH_4) and ammonia (NH_3) emissions. Production of higher levels of total ammonia-nitrogen (TAN) during the acidogenesis due to the high nitrogen (N) contents in swine manures significantly reduce the CH_4 yield. Australian zeolites have a high adsorption capacity of ammonium (NH_4^+).Therefore; reduction of N during the AD through zeolite not only improves the CH_4 production but also reduces potential environmental risks associated with NH_3 emissions from swine manure. This study is aimed at determining the optimum Australian zeolite dose that produces maximum TAN recovery at optimum CH_4 production. Swine manure was treated with natural and sodium zeolites at 0, 10, 40, 70, 100mg/L and digested anaerobically for 60 days. Natural zeolites at a dose of 40g/L resulted in the highest increase (29%) in total CH_4 yield from swine manure compared to the untreated manures, while natural and sodium zeolites at a dose of 100g/L reduced 50% and 52% of NH_4^+ in the medium respectively, compared to the control. However, the increases in CH_4 yield under those two treatments were only 10% and 12%.

Key Words: ammonium inhibition, adsorption, biogas, cations, natural zeolite, sodium zeolite

Introduction

Excessive atmospheric nitrogen (N) levels and consequential increases in deposition is a major global environmental and ecological concern (UNEP, 2014). Ammonia emissions significantly contribute to atmospheric N load and those emissions are in the same order of magnitude as of N_xO-N emissions in parts of the word (Asman et al., 1998). Globally, livestock production accounts for 64% of NH_3 emissions of cumulated GHG (FAO, 2006). Swine farming contributes to about 9% of livestock related NH_3 emissions which are about 668 million tonnes CO_2-eq (FAO, 2011). In swine industry, about 50% of NH_3 emissions are from manure/slurry storage and pig housing. The rest includes the emission associated with land application of manures (Portejoie et al., 2003). However, in the circumstance of GHG mitigation, NH_3 emissions cannot be considered independently from CH_4 emissions and energy production related to manure management (Petersen and Sommer, 2011). In terms of reducing CH_4 emission and increasing green energy production, anaerobic digestion (AD) is one of the environmentally sustainable best management practices for handling livestock manures and other organic waste materials (Maria et al., 2013). About 80% of organic-N in the feedstock is transformed into NH_4^+ and NH_3 forms (total ammonia nitrogen = TAN) (Sommer et al., 2013). AD process primarily removes carbon from the medium, additional processes are required to remove N from the digested effluents before it discharges to the environment to minimize adverse impacts such as GHG emission. The other disadvantage of accumulation of TAN within the digester is its inhibitory effects on anaerobic micro-organisms leading to significant reduction in methanogenesis (Hansen et al., 1998). Further, combining the nitrogen removal process with a recovery during AD would maximise environmental and economic outcomes from agricultural waste management. Previous research demonstrated that natural ion-exchange materials with high cation adsorptive capacity and NH_4^+ selectivity, such as zeolites have a potential in nitrogen removal from organic slurries and addressing NH_4^+ inhibition during AD resulting enhanced biogas yields (Montalvo et al., 2012). At the end of the process, NH_4^+ enriched zeolites can be used as slow releasing fertilizer (Li et al., 2013). However, past research primarily focused on mixing zeolite into the digestive feedstock with the aim of enhancing only the CH_4 production rather than maximising both TAN and CH_4 recovery. Therefore, the main objective of this study is to determine the optimum zeolite doses that maximise TAN recovery with enhanced CH_4 production. This study used Australian natural zeolites and sodium chloride modified zeolite (sodium Zeolite).

Methods

This mesophilic anaerobic digestion experiment was conducted as a batch trial using 400 mL (working volume) mini-glass digesters. The inoculum (from Berrybank farm, Windermere, Victoria) and swine manure (from the University of Melbourne) were added into the digesters at a ratio of 1:1 volatile solids (VS) / basis. The characteristics of inoculum and swine manure are shown in Table 1.

Table 1: Characteristics of swine manure and inoculum used for the experiment

Parameter	Swine manure	Inoculum
TS%	7 (0.15)	3 (0.01)
VS%	69 (0.32)	67 (0.19)
pH	6.73 (0.05)	7.39 (0.01)
Alkalinity (mg/L)	2500 (115)	4033 (44)
sCOD (mg/L)	14725 (214)	1734 (35)
BOD (mg/L)	1991 (31)	204 (42)
NH_4-N (mg/L)	664 (12)	1298 (9)
N%	2.48 (0.02)	2.97 (0.02)
C%	33.54 (0.13)	31.76 (0.16)

SE within brackets (n = 3)

The inoculum was incubated 14 days at 37°C until removing all available VS prior to the experiment. The contents were treated with four different doses (10, 40, 70, and 100 [g/l]) of Australian natural zeolite (from Zeolite Australia Private Limited, Werris Creek, NSW) and sodium zeolite (prepared as described in (Wijesinghe et al., 2016) separately. Controls for each material were also maintained and all treatments were replicated three times. The headspace of each digester was flushed with Nitrogen gas to create an anaerobic environment in digesters. The digesters were kept in an incubator at a constant temperature of 37°C and manually shaken daily to mix the content.

Data collection and analysis

The volume of biogas generated was measured daily using a 1L syringe (Hamilton Super Syringe). CH_4 concentrations in biogas were analysed using gas chromatography (GC Agilent 7890). NH_4^+ concentrations of digestate at the end were analysed with segmented Auto analyser (Skalar SAN^{++}).
Statistical analysis of results was made with Two-way analysis of variance (ANOVA) following a General Linear Model (GLM) with Minitab V17, statistical software. Fisher's LSD test was employed for comparing treatment means.

Results

Effect of zeolites on gas production:

Figure1 and 2 show the final biogas volume and CH_4 production respectively for different natural and sodium zeolite doses. Zeolite doses have significant relationship ($p < 0.001$) with biogas production and not with the type of zeolites ($p = 0.104$), both zeolite types ($p = 0.013$) and zeolite doses ($p < 0.0001$) have significant relationship with CH_4 production. However, the significant interaction ($p < 0.0001$) indicates that the relationship between zeolite types and biogas and CH_4 production depends on the zeolites doses. The Fisher's tests revealed significant differences between the biogas yields and CH_4 yield of all natural and sodium zeolites digesters compared to the yields of no zeolites digesters (control). Both final biogas production and CH_4 production were increased with increasing natural zeolite dose up to 40g/L of digestate and decreasing towards 100 g/L. Application of sodium zeolites shows lower enhancement of biogas and CH_4 production compare to the natural zeolite up to 40 g/L. At the dose of 70g/L zeolites, sodium zeolites show higher gas production than the same rate of natural zeolite and at 100g/L, both biogas and CH_4 production were quite similar. Natural zeolites rate at 40g /L shows 29%, the maximum CH_4 production. However, CH_4 production increased over 10% compare to the control at all doses of natural and sodium zeolites (Table 3).

Table 3: Summary of percentage of CH_4 enhancement and NH_4^+ reduction at different rates of zeolites application

Type of Zeolite	10 g/L		40g/L		70 g/L		100 g/L	
	Enhanced % of CH_4	Reduced % of NH_4^+	Enhanced % of CH_4	Reduced % of NH_4^+	Enhanced % of CH_4	Reduced % of NH_4^+	Enhanced % of CH_4	Reduced % of NH_4^+
Natural Zeolite	15 (1.4)	5 (4.7)	29 (1.05)	20 (4.4)	13 (0.85)	37 (3.19)	10 (1.33)	50 (2.18)
Sodium Zeolite	13 (1.21)	4 (0.75)	15 (0.18)	19 (1.38)	18 (0.89)	31 (1.11)	12 (0.16)	52 (0.83)

SE within brackets (n = 3)

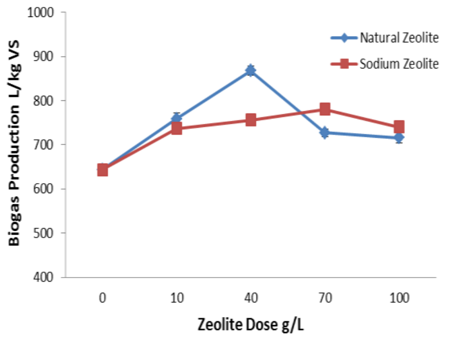

Figure1: Biogas production with zeolite doses

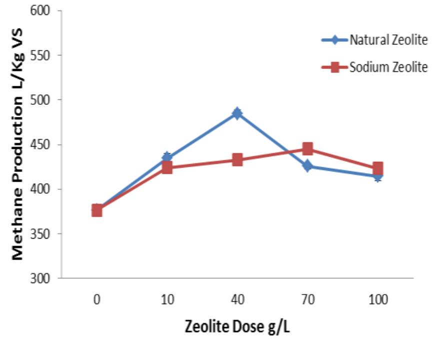

Figure 2: Methane production with zeolite Dose

Effect of zeolite on ammonia concentration inside the digester

Figure 3 shows the NH_4^+ concentration inside the digesters with different rates of zeolites at natural and sodium zeolites. According to the two-way ANOVA, only zeolite's doses have a statistically significant relationship with NH_4^+ concentration ($p < 0.001$). The Fisher's tests revealed significant differences between the NH_4^+ concentration except natural and sodium zeolites digesters at the rate of 10g/L compared to the NH_4^+ concentration of the no zeolite digesters. However, there are no significant differences between NH_4^+ concentration and the same rate of natural and sodium zeolite digesters and the removal of NH_4^+ increased with the increasing of zeolite dose at both natural and sodium zeolites (Figure 3 & Table 3)

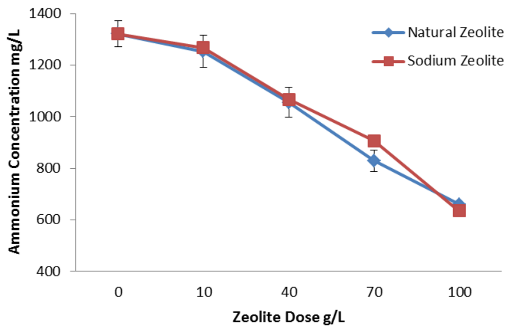

Figure 3: Ammonium concentration inside the digesters with natural and sodium zeolites at different doses

Discussion:

Enhancement of CH_4 production from N rich organic substrates through AD due to zeolites addition could primarily be attributed to favourable free ammonium N (FAN)/NH_4^+-N equilibrium in the medium in the presence of zeolite, a material which has the capacity to adsorb free NH_3 and NH_4^+ ion from the digestate (Milan et al., 2001). Although the increase in CH_4 was observed up to the 40g/L rate of zeolites, higher doses beyond that resulted in a decline in the increases in CH_4 production. It could be speculated that immobilisation of NH_4^+ than necessary optimal levels with higher doses of zeolites acted as a capacity constraint in the system. Further, zeolites additions into the digesters might have increased the total solids content result in a relative reduction in, free available water inside the digesters. This might have affected the transport of nutrients and metabolites in the vicinity of the zeolite particle and the microorganisms associated (Milan et al., 2001). In addition, a change of NH_4^+, NH_3 equilibrium in the digestate affected the AD process performance. The NH_4^+ concentration inside the digesters decreased with increasing zeolite dose. The addition of natural zeolites reduces NH_4^+ in the solution by releasing Mg^{2+}, Ca^{2+} and Na^+ ions. Sodium zeolites adsorb NH_4^+ by releasing mainly Na^+ (Lin et al., 2013). The optimum levels of these cations stimulate microbial growth and they are antagonistic to NH_4^+ inhibition, however, a higher level of these cations are toxic to AD process (Chen et al., 2008). Variation of the amount of these cations might be another reason for biogas and CH_4 yield variation within the treatments. Previous studies indicated that sodium zeolites adsorbed 25% more NH_4^+ than natural zeolites at 1000 mg-N pure NH_4Cl solution (Wijesinghe et al., 2016), however, the present study did not show a significant difference in NH_4^+ adsorption. The reason for this observation; (a) Natural zeolite has relatively more exchangeable Ca^{2+}, it could be assumed that during the process Ca^{2+} precipitated with other anions, especially carbonates, in the medium (a process encouraged at pH > 7) resulting in a higher NH_4^+ adsorption (Lin et al., 2014), (b) it could be that Na^+ present in the digestate, might have enhanced NH_4^+ adsorption via the two-step process given the in the equations 1 and 2 below (similar to the formation of sodium zeolites). However, these processes need to be confirmed through further research.

$$Zeolite - C^{n+} + nNa^+ \rightarrow Zeolite - (Na^+)_n + C^{n+} \qquad \text{Eq.1}$$

$$Zeolite - (Na^+)_n + nNH_4^+ \rightarrow Zeolite - (NH_4^+)_n + nNa^+ \qquad \text{Eq.2}$$

Conclusion

This research confirmed that zeolites are effective in adsorbing NH_4^+ from aqueous mediums. Further, the study demonstrated that that Australian zeolite either in natural or sodium chloride treated form significantly enhance biogas production from swine manure through AD; while adsorbing substantial quantity of NH_4^+ from the medium during the process. The effects of natural and sodium zeolites were similar in the current study. Total NH_4^+ adsorption by zeolites appeared positively correlated with biogas/CH_4 production supporting the proposition that reduction in soluble NH_4^+ levels in AD medium favours methanogenesis process. Although the higher doses of zeolite continued to reduce NH_4^+– N linearly, the increases in CH_4 yield were marginal at doses above 40g/L. Further research is essential to understand and improve the efficiency of the AD process.

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