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Int. Agrophys., 2013, 27, 169-173
doi: 10.2478/v10247-012-0082-y

Zeolite and swine inoculum effect on poultry manure biomethanation

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Received May 16, 2012; accepted October18, 2012

A b s t r a c t. Poultry manure is an ammonia-rich substrate that inhibits methanogenesis, causing severe problems to the anaerobic digestion process. In this study, the effect of different natural zeolite concentrations on the mesophilic anaerobic digestion of poultry waste inoculated with well-digested swine manure was investigated. A significant increase in methane production was observed in treatments where zeolite was added, compared to the treatment without zeolite. Methane production in the treatment with 10 g dm^{-3} of natural zeolite was found to be 109.75% higher compared to the treatment without zeolite addition. The results appear to be influenced by the addition of zeolite, which reduces ammonia toxicity in anaerobic digestion and by the ammonia-tolerant swine inoculum.

K e y w o r d s: poultry manure, zeolite, swine manure inoculum, ammonia inhibition, anaerobic digestion

INTRODUCTION

Poultry farming became one of the most intensive branches of livestock production in modern agriculture. The consequence of this intensive production is generation of large amounts of wastes (Sakar *et al*., 2009). Poultry manure contains a high fraction of biodegradable organic matter and therefore their disposal without treatment causes adverse environmental impacts (Ogunwande *et al*., 2008). Among the different methods that have been used to treat poultry wastes, anaerobic digestion has been recommended by many authors (Ardic and Taner, 2005; Yilmazel and Demirer, 2011). Anaerobic digestion is a widely applied method in which anaerobic bacteria and archaea degrade complex organic material to biogas (Angelidaki *et al*., 2011). However, poultry manure is a substrate rich in total ammonia (ammonium + free ammonia) which, in high concentrations, is a well-known inhibitor of methanogenesis. Ammonia is produced by the biological degradation of nitrogenous matter, mostly in the form of proteins (Chen *et al*., 2008). It has been established that ammonia toxicity is mainly caused by the free ammonia concentration in the substrate (Chen *et al*., 2008). According to the literature, free ammonia concentrations above 100 mg NH_3-N dm^{-3} are able to inhibit unacclimated methanogenic cultures to elevated ammonia levels (Kotsopoulos *et al*., 2008). The free ammonia concentration in a substrate is mainly affected by pH, temperature, the total ammonia concentration, and the total gas pressure (Bonmatí and Flotats, 2003; Nielsen and Angelidaki, 2008). Finally, it is generally accepted that when the total ammonia exceeds 4 g NH_4^+-N dm^{-3}, methanogenesis is inhibited regardless of free ammonia levels (Nakakubo *et al*., 2008).

A common solution to eliminate ammonia inhibition during the anaerobic digestion of poultry manure is the dilution of the substrate to 0.5-3.0% of total solids (Bujoczek *et al*., 2000). However, the final large amount of wastes to be treated renders this solution as economically unattractive. An alternative way to avoid ammonia toxicity is the addition of clay mineral compounds, such as bentonite and natural zeolite. Zeolite has the ability to entrap or release various cations due to its high cation exchange capacity (Venglovsky *et al*., 2005). A number of researchers have reported that the addition of zeolite in wastes reduces the inhibitory effect of free ammonia (Kotsopoulos *et al*., 2008; Milán *et al*., 2011).

Inocula and the respective methanogens derived from bioreactors fed with substrates rich in ammonia (such as swine manure) are more tolerant to the ammonia inhibition effect (Chen *et al*., 2008). However, up to now, the effect of zeolite on the mesophilic anaerobic digestion of poultry manure in combination with well-digested swine manure used as an inoculum has not been previously investigated.

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The aim of this study was to investigate the effect of different natural zeolite concentrations on the mesophilic anaerobic digestion of poultry waste. Furthermore, an additional aim was to examine the use of an ammonia-acclimated inoculum together with zeolite in order to provide a potential solution to the ammonia inhibition effect on methanogenesis from poultry manure.

MATERIALS AND METHODS

The natural zeolite used in the experiments was obtained from Xerovouni location of the Avdella Area (Prefecture of Evros, Greece). The chemical and mineralogical composition of the zeolite is given in Table 1 (Tzamos *et al.*, 2011). The zeolite had a particle size less than 2.0 mm.

Raw poultry manure was collected from a poultry farm, located in Neochorouda of Thessaloniki, Greece. The manure was diluted with distilled water to obtain a waste with a total solid concentration around 5%. This was done, as there have been reports that fresh poultry manure diluted to 5% of total solids accounts for the highest methane production (Bujoczek *et al.*, 2000). The characteristics of the poultry manure used in the experiment are shown in Table 2.

The inoculum used was well-digested swine manure derived from a mesophilic anaerobic digester (3 000 cm^3 working volume; operating temperature: 36±1°C). The inoculum had a pH value equal to 7.50, and the total solids (TS) and volatile solids (VS) contents were 13.36 and 7.57 g dm^{-3}, respectively.

Four batch experimental treatments were carried out in duplicate for the purpose of this research work. The four experimental treatments were:

– Z_0 (control): two batch reactors with inoculum and poultry manure without zeolite addition,
– Z_5: two batch reactors with inoculum and poultry manure and 5.0 g zeolite dm^{-3} of waste,
– Z_{10}: two batch reactors with inoculum and poultry manure and 10.0 g zeolite dm^{-3} of waste,
– Z_b (blank): two batch reactors with inoculum and water only, without poultry manure and zeolite, for estimation of background CH_4 production from the inoculum.

The total volume and the working volume of each reactor were 1 000 and 900 cm^3, respectively. Each reactor was equipped with a magnetic stirring device. The reactors were placed in an incubator, which was controlled at 36±1°C using a thermostat. The experimental setup is shown in Table 3.

During the experiment, the following parameters were measured according to APHA (2005): TS, VS, pH, chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and organic nitrogen and ammonia concentrations. Volatile fatty acid (VFA) was measured with a gas chromatograph (HP 5890 series II) equipped with a flame ionization detector (FID) (Kotsopoulos *et al.*, 2009). The free ammonia concentration was calculated as previously described by Bonmatí and Flotats (2003). Gas production was monitored daily by the water displacement method. The percentages of methane and CO_2 in the gas mixture were determined daily, using a gas separator containing an alkaline solution (3% NaOH) (Kougias *et al.*, 2010). All the analyses were made in triplicate (n=3) and the standard deviation (SD) is presented.

T a b l e 1. Chemical and mineralogical composition of zeolite

Chemical composition		Mineralogical composition	
Oxides	% mass	Minerals	% mass
SiO_2	72.96	HEU - type zeolite	54
TiO_2	0.09	Mica	4
Al_2O_3	11.93	Smectite	6
Fe_2O_3	1.20	Alkali feldspar	8
MnO	0.09	Plagioclase	9
MgO	1.04	Quartz	8
CaO	2.77	Cristobalite	11
Na_2O	1.29		
K_2O	1.89		
Loss on ignition	7.61		

T a b l e 2. Characteristics of poultry manure used in the experiment (n=3, SD)

Parameters	Value
pH	6.85±0.03
Total solids (g dm^{-3})	43.8±0.13
Volatile solids (g dm^{-3})	22.8±0.07
Total Kjeldahl nitrogen (g N dm^{-3})	5.45±0.18
Total ammonia (NH_4^+) (g N dm^{-3})	4.73±0.12

T a b l e 3. Experimental set-up for batch digesters

Treatment	Raw materials added			
	Inoculum	PM [4] (cm^3)	Zeolite (g)	Distilled water (cm^3)
[1]Z_0	90	810	0	0
[2]Z_5	90	810	4.5	0
[2]Z_{10}	90	810	9	0
[3]Z_b	90	0	0	810

[1]Z_0 (control), designates the absence of zeolite in the reactors; [2]Z_5 and Z_{10}, designate the doses of zeolite which were 5.0 and 10.0 g zeolite g dm^{-3} of waste, respectively; [3]Z_b (blank), designate the presence of only inoculum and water only in the reactors; [4]PM, poultry manure.

RESULTS AND DISCUSSION

Poultry manure contains a high concentration of ammonia, therefore, direct anaerobic digestion of poultry manure has been characterised as extremely problematic. Nowadays, the most common approach to treat poultry manure anaerobically is to co-digest it together with ammonia-free substrates (Sakar *et al.*, 2009). However, ammonia-free substrates are either site-specific or seasonable. Therefore, an efficient direct anaerobic digestion method of poultry manure has to be developed. The present study investigated the mesophilic anaerobic digestion of poultry manure by the addition of different amounts of natural zeolite.

The accumulated biogas production is illustrated in Fig. 1. The overall digestion process periods for treatments Z_5 and Z_{10} were almost the same, lasting 42 and 44 days, respectively. As can be seen, the addition of zeolite in the substrate enhanced biogas production. In the Z_{10} treatment, where 10 g dm^{-3} zeolite was added, the biogas production was increased by 109.75 and 13.92%, compared with the Z_0 and Z_5 treatments, respectively. In addition, in the control Z_0 treatment, where no zeolite was added, two periods with no biogas production were observed, indicating an extremely strong inhibition effect of ammonia. The first period lasted approximately from the 5th to the 24th day and the second period from the 30th day till the end of the digestion process. Moreover, since the ammonia concentration in raw poultry manure was high, the ammonia tolerant inoculum positively affected the anaerobic digestion process; even in the control treatment, where no zeolite was added (Z_0), methanogenesis was initiated at the same time as in the two treatments where zeolite was added (Z_5 and Z_{10}). This result coincides with a previous study, where it was demonstrated that digested swine manure inocula were tolerant to ammonia toxicity (Kotsopoulos *et al.*, 2008). Methane production in the Z_b experimental treatment was below detection limits during the experimental period.

Salminen and Rintala (2002) reported that the maximum biogas yield from poultry manure in terms of volatile solids is 340-495 cm^3 g^{-1} VS, with a 58.6% mean methane concentration in the biogas. In this experiment, the methane yield of volatile solids was 121.96, 228.93, and 268.22 cm^3 g^{-1} VS added in the Z_0, Z_5, and Z_{10} treatments, respectively (Table 4). Treatments Z_5 and Z_{10} had 79 and 92% of the maximum potential methane yield of poultry manure, respectively. In contrast, when biogas production ceased in treatment Z_0, the methane yield was only 42% of the maximum potential. In addition, the volatile solids reduction was 41.9, 61.4, and 77.4% in the Z_0, Z_5 and Z_{10} treatments, respectively (Table 4). These results indicate that the addition of zeolite (up to 10 g dm^{-3}) has a positive impact on the degradation of organic matter and, consequently, on the methane yield. Also in a previous study, it has been mentioned that the addition of clay minerals during anaerobic digestion reduced the inhibitory effect of ammonia; hence, the amount of methane production was increased (Kotsopoulos *et al.*, 2008). This could be explained by the ability of zeolite to reduce the ammonium concentration *via* ion exchange (Montalvo *et al.*, 2012). Consequently, the concentration of free ammonia is also reduced due to the equilibrium between ammonium ions and free ammonia in the substrate (Montalvo *et al.*, 2006). Additionally, the comparison of the methane yields of Z_5 and Z_{10} suggests that the zeolite concentration during anaerobic digestion of poultry manure is a key factor of efficient biogas production as it is with other ammonia rich waste (Montalvo *et al.*, 2012).

The total VFA concentrations as well as the pH values for the Z_0, Z_5 and Z_{10} treatments at the end of the digestion processes are presented in Table 5. The total VFA concentration was 10.80, 3.29, and 1.08 g dm^{-3} in the Z_0, Z_5 and Z_{10}

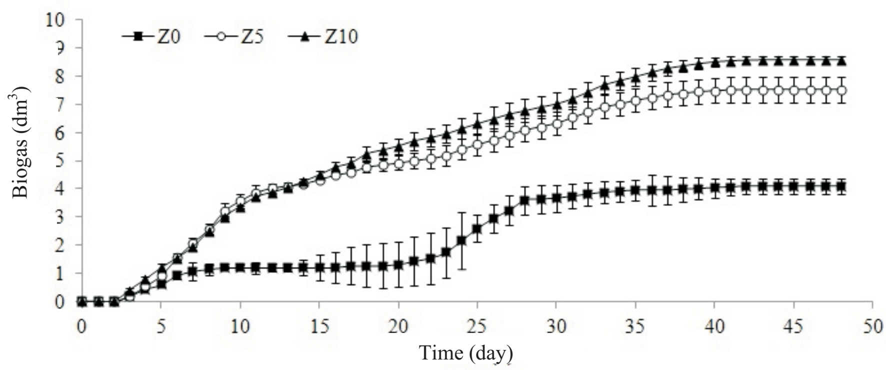

Fig. 1. Accumulated biogas production in all the treatments. The bars designate the values of the two replicates of each treatment.

T a b l e 4. Methane yields and the reduction of volatile solids in the examined treatments (n=3, SD)

Treatment	Methane yield (cm^3 CH_4 g^{-1} VS added)	VS reduction (%)
[1]Z_0	121.96±3.94	41.92±1.36
[2]Z_5	228.94±2.03	61.42±3.90
[2]Z_{10}	268.23±2.25	77.39±1.50

Explanations as in Table 3.

treatments, respectively. It should be noticed that the accumulation of VFAs in treatment Z_0 was very high and, consequently, the pH value exhibited lower levels than in treatments Z_5 and Z_{10}. The increase in the VFA concentration in a biogas process is well known due to process imbalance, thus it has been suggested as an indicator of optimal anaerobic digestion (Boe *et al*., 2007). In contrast, the accumulation of VFAs appeared in the lower concentration in the Z_{10} treatment. As for the pH, it was demonstrated that the values in all the cases remained within the optimum range for the biomethanation process (Angelidaki *et al*., 2011). Nevertheless, the pH levels in Z_{10} were lower compared to the pH levels reported in a previous research (Milán *et al*., 2001), where addition of 10 g of zeolite dm^{-3} of waste increased the pH value to 8.1.

At the end of the biomethanation processes, a deviation in the ammonia concentration among the experimental treatments was found (Fig. 2). The ammonia concentration was decreased in accordance with the zeolite concentrations in the batch reactors. This could be explained by the different efficiency of anaerobic digestion between the treatments resulting in different levels of utilization of organic nitrogen compounds (proteins, amino acids, amines, and urea) during anaerobic metabolism as described before by Milán *et al*. (2001). It has been observed that the zeolite adsorption process leads to reduction of ammonium ions in treatments Z_5 and Z_{10} up to 58 mg NH_4^+-N g^{-1} zeolite. Jung *et al*. (2004) have reported similar levels (50-60 mg NH_4^+-N g^{-1} zeolite) of ammonium ion absorption using a modified batch reactor. The presence of natural zeolite in the reactors maintained the ammonia concentration at levels that did not inhibit methane production (Table 5). At the end of the experimental period, the free ammonia concentration in the Z_0 treatment was calculated to be lower, compared to that in Z_5 and Z_{10}. This could be explained by the strong ammonia inhibition effect on methanogenesis that led to VFA accumulation in the digester, causing a drop in the pH value, as described previously (Chen *et al*., 2008). Nevertheless, the absorption of ammonium in treatments Z_5 and Z_{10} by the addition of zeolite was not so extensive enough to explain fully the significant differences in the methane yields in treatment Z_0. It has been reported by Kotsopoulos *et al*. (2008) that a possible explanation is that zeolite improved anaerobic digestion also by influencing the microbial and enzymatic transformations of a variety of other substances. Another possible explanation could be that zeolite provides methanogenic populations with a high-capacity immobilisation matrix (Milán *et al*., 2001; Montalvo *et al*., 2005).

Finally, 10 g zeolite dm^{-3} was the dose which had the best results in mesophilic biomethanation of poultry manure inoculated with well digested swine manure. This indicates that the combination of zeolite and ammonia acclimatized inocula could provide a potential solution to the ammonia toxicity effect on methanogenesis from poultry manure.

T a b l e 5. VFA concentration and pH values for each treatment (n=3, SD)

Treatment	Total VFA ($mg\ dm^{-3}$)	pH
$^1Z_0$	10.806±0.001	7.14±0.02
$^2Z_5$	3.298±0.000	7.76±0.04
$^2Z_{10}$	1.077±0.000	7.79±0.02

Explanations as in Table 3.

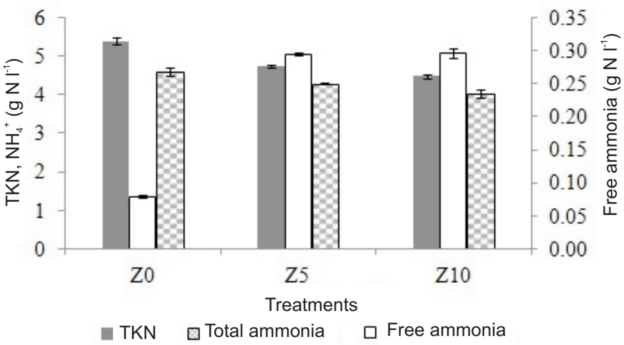

Fig. 2. TKN, total ammonia, and free ammonia concentration for each treatment.

CONCLUSIONS

1. The addition of 5 and 10 g zeolite dm^{-3} poultry manure enhanced the biogas production during the anaerobic mesophilic digestion, compared with the control treatment, where no zeolite was added.

2. The best environmental results were observed at the treatment with 10 g zeolite dm^{-3} manure. The volatile solid reduction and the energy recovery from the degradation of organic matter were presented at higher levels, than in the other tested treatments.

3. The zeolite adsorption process led to a reduction of ammonium ions in treatments Z_5 and Z_{10} up to 58 mg NH_4^+-N g^{-1} zeolite.

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