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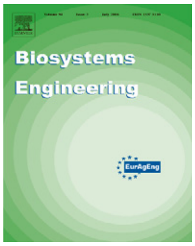

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The impact of different natural zeolite concentrations on the methane production in thermophilic anaerobic digestion of pig waste

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The effect of natural zeolite on the thermophilic anaerobic decomposition of pig waste was investigated. In particular, the effect of adding different amounts of zeolite on the increase of methane production of waste was examined. Two sets of experiments were carried out in duplicate: one with a low initial concentration of organic matter and one with a high initial concentration of organic matter. These experiments were carried out in eight batch reactors at 55 °C. The doses of zeolite which were used for the experiments were 0, 4, 8, 12 $g\,l^{-1}$ of waste. Methane production was significantly higher in treatments with natural zeolite at doses 8 and 12 $g\,l^{-1}$ of wastes, compared to those without zeolite. Also in treatments with natural zeolite, the reduction of volatile solids and biological oxygen demand (BOD_5) was statistically significant. The results appear to be caused by the addition of zeolite, which adsorbs ammonia, thus having an effect not only on the toxicity of ammonia and on the C/N proportion but also on the regulation of acidity (pH) of the pig wastes.

1. Introduction

Pig farms generate large amounts of waste with a high concentration of organic matter, nutrients, trace elements and a variety of pathogenic factors (Venglovsky *et al.*, 2005). Because of the high organic matter concentration in pig wastes, disposal of pig wastes without treatment causes major environmental problems. Among the different methods that have been used to treat pig wastes, anaerobic digestion has been recommended by many authors (Milán *et al.*, 2001; Hartmann & Ahring, 2005; Murto *et al.*, 2004). Anaerobic digestion is a complex process in which anaerobic bacteria decompose organic matter in the absence of oxygen. Anaerobic digestion produces biogas, reduces odour and the digested residues, which are rich in inorganic nutrients, and are suitable for use as fertilisers (Sahlström, 2003).

Biogas production under thermophilic conditions is a preferred choice to treat animal manure due to their evident advantages such as shorter hydraulic retention time (HRT), improved sanitary effects and better pathogen destruction than mesophilic digestion (Dugba & Zhang, 1999; Sahlström, 2003). However, anaerobic degradation of pig manure at thermophilic temperatures has been proven to be difficult

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Nomenclature

BOD_5	biochemical oxygen demand, $mg\,l^{-1}$
HRT	hydraulic retention time, d
K_α	acid ionisation constant for ammonia
$N\text{-}NH_3$	ammonia nitrogen, $mg\,l^{-1}$
SD	standard deviation
T	temperature, °C
TKN	total kjeldahl nitrogen, $mg\,l^{-1}$
TS	total solids, $mg\,l^{-1}$
VS	volatile solids, $mg\,l^{-1}$

(Hansen *et al.*, 1998). This is mainly due to the ammonia inhibition (Sung & Liu, 2003).

Ammonia is produced during the anaerobic degradation of organic matter, which is rich in protein and urea, such as pig wastes. It has been reported that if ammonia concentration is high, it can inhibit methanogenesis (Hansen *et al.*, 1998). Ammonia toxicity is related to the free ammonia concentration. Furthermore, free ammonia concentrations (100–150 mg $[N]\,l^{-1}$) cause inhibition in unadapted cultures (Braun *et al.*, 1981; De Baere *et al.*, 1984). According to Kugelman and McCarty (1965), a concentration of $150\,mg\,l^{-1}$ free ammonia could be toxic at pH values close to 8. In order to avoid the negative effect of free ammonia on the anaerobic degradation, its concentration should be less than $80\,mg\,l^{-1}$ (Marchaim, 1992). Free ammonia concentration depends on pH, temperature and total ammonia concentration (Bonmatí & Flotats, 2003). The free ammonia concentration increases with increasing temperature or pH. This explains why several authors have found that anaerobic digestion of pig wastes is more easily inhibited at thermophilic temperatures rather than at mesophilic temperatures (Braun *et al.*, 1981; Chen & Day, 1986; Hansen *et al.*, 1998).

The ratio C/N plays an important role on the anaerobic degradation. Bacteria need nitrogen to construct their cell structure and carbon as an energy source. It has been reported that a favourable ratio for anaerobic digestion of pig wastes should be 16 (Sievers & Brune, 1978). However, in pig wastes, the ratio is less than the optimum and this causes anaerobic process instability with poor methane production. To improve the C/N ratio in pig wastes, several authors have used co-digestion of pig wastes with wastes high in carbon content (Murto *et al.*, 2004; Kaparaju & Rintala, 2005).

Angelidaki and Ahring (1993) have used bentonite and bentonite-bound oil (BBO) to improve the anaerobic thermophilic digestion of cattle waste. They found that the major effect of bentonite and BBO was not through a direct chemical binding of ammonia by bentonite, but through an increasing resistance to ammonia inhibition. Furthermore, it has been reported that the addition of activated carbon or glauconite or both of these in pig waste rich in ammonia improves the thermophilic anaerobic digestion and also increases the methane production (Hansen *et al.*, 1999).

Some researchers used zeolite to avoid the inhibition effect of ammonia on the anaerobic digestion of pig wastes (Milán *et al.*, 2001; Montalvo *et al.*, 2006; Sánchez *et al.*, 1995). All the previous researchers have used zeolite to improve anaerobic digestion at the mesophilic range. Zeolite has the ability to preferentially remove ammonium ions from wastewater (Jung *et al.*, 2004; Sarioglu, 2005). Zeolites are minerals which have the ability to entrap or release various cations through ion –exchange reaction and adsorption (Venglovsky *et al.*, 2005).

In the present study, the impact of different concentration of natural zeolite on thermophilic anaerobic digestion of pig wastes was examined.

2. Materials and methods

2.1. *Natural zeolite*

The natural zeolite used in the experiments was obtained from a deposit located in the Prefecture of Evros, Greece. The chemical and mineralogical composition of the zeolite is given in Table 1 (Sikalidis, 1998). The zeolite had a particle size less than 2.0 mm.

2.2. *Pig waste*

Waste used in the experiments was from a pig farm which was located near the laboratory (Thermi City, Greece). The characteristics of pig waste used in the experiments are given in Table 2.

2.3. *Analyses*

Biochemical oxygen demand (BOD_5); Total solids; Volatile solids; Total kjeldahl nitrogen; Ammonia nitrogen and pH were determined in both the influent and effluent of anaerobic reactors. Two samples of waste were collected each time for analysis and analyses were carried out according to standard methods for the examination of water and wastewater (APHA (American Public Health Association), 1995). The calculation of free ammonia concentration was based on the following equation (Anthonisen *et al.*, 1976)

$$\frac{Free-NH_3}{Total-NH_3}=\frac{10^{pH}}{10^{pH}+1/K_\alpha}=\frac{10^{pH}}{10^{pH}+e^{6344/(273+T)}},$$

where *Free*-NH_3 is the free ammonia concentration, *Total*-NH_3 is the total ammonia concentration, K_α is the acid ionisation constant for ammonia and T is the temperature in °C.

Gas production was monitored daily by water displacement using 4.5 l reservoirs connected to the reactors. The percentages of methane and CO_2 were determined using a gas chromatograph (Varian 3700) equipped with a thermal conductivity detector (TCD). Two columns, Porapak Q and Molecular Sieve 5A, were used in a series/bypass arrangement for the complete separation of the gases (Lemonidou *et al.*, 1998).

Table 1 – Chemical and mineralogical composition of zeolite

Chemical composition		Mineralogical composition	
Oxides	% wt	Minerals	%
SiO_2	70.23	Clinoptilolite (Na, K)$_6$Al$_6$Si$_{30}$O$_{72}$20H$_2$O	
Al_2O_3	11.15		59
CaO	3.38	K, Na-Feldspar	8
K_2O	3.28	Plagioclase	7
Na_2O	1.11	Quartz	5
MgO	0.6	Christobalite	6.5
Fe_2O_3	0.64	Calcite	3
TiO_2	0.07	Dolomite	1.5
MnO_2	0.02	Clays (total)	9
P_2O_5	0.01		
Loss of ignition	9.51		

Table 2 – Characteristics of pig wastes used in the experiments

Parameter[b]	VS1[a]		VS2		
	Mean	S.D.	Mean	S.D.	Sig.
TS, $mg\,l^{-1}$	11 540.43	977.085	14 981.87	1011.35	0.000*
VS, $mg\,l^{-1}$	7810.00	679.13	11 637.87	694.60	0.000*
BOD_5, $mg\,l^{-1}$	6861.87	530.28	10 246.87	557.51	0.000*
TKN , $mg\,l^{-1}$	567.3125	56.08371	570.06	75.46	0.869
N-NH_3, $mg\,l^{-1}$	274.94	25.61	239.62	23.24	0.000*
pH	6.97	0.064	7.04	0.0484	0.003*

Values are mean of 32 determinations on different samples of waste.

*The mean difference is significant at the 0.05 level (t-test).

[a] VS1, Waste with a low initial concentration of organic matter; VS2, Waste with a high initial concentration of organic matter.

[b] TS, total solids; VS, volatile solids; BOD_5, biochemical oxygen demand; TKN, total kjeldahl nitrogen; N-NH_3, ammonia nitrogen; SD, standard deviation; Sig., significant.

Data analysis was performed using SPSS version 11.5. Significant differences ($p<0.05$) in the previous parameters among treatments were based on one-way ANOVA (Analysis Of Variance). Where differences were found, the Duncan test was used to identify which treatments were significantly different. Differences in pig waste characteristics between experiments (VS1, VS2) were evaluated by using a *t*-test.

2.4. *Experimental set-up and operation*

Two sets of experiments were carried out in duplicate. The first experiment was carried out with a low initial concentration of organic matter (VS1) and the second was carried out with a high initial concentration of organic matter (VS2), as shown in Table 2. Experiments were carried out in eight batch reactors with a working volume of 1.25 l each. Each reactor was equipped with a stirring device. The reactors were placed in an oven which was controlled at 55 °C. Two preliminary measurements were conducted in order to be used for the design of the experiments. The duration of each preliminary measurement was 30 days. The results of the above measurements were used as guides for the amounts of zeolite which were used in the experiments, and for the duration of each set. Preliminary experiments show that the anaerobic process was practically ceased in 15 days, and obvious differences in biogas production among treatments appeared at zeolite doses 0, 4, 8, and 12 $g\,l^{-1}$ (data not presented). It was decided that the duration of each set would last 15 days, as it was defined by the results of the preliminary measurements. The number of treatments was four for each set; each treatment was carried out by duplicate. The doses of zeolite used in the experiments were 0, 4, 8, and 12 $g\,l^{-1}$ waste and each treatment was designated Z_0, Z_4, Z_8, and Z_{12}, respectively.

3. Results

Table 3 shows the volatile solids removal percentage obtained from all the systems under study. Increasing the zeolite dose from 0 to 8 $g\,l^{-1}$ increased the removal of volatile solids from 26.04% to 69.33% in the VS1 experiment and from 38.58% to

Table 3 – Volatile solids and BOD_5 removal percentage, % achieved at the end of the batch process in VS1 and VS2 experiments

Parameters	Experiment	Treatments			
		Z_0	Z_4	Z_8	Z_{12}
Volatile solids	VS1	26.04 ± 7.65^a	43.57 ± 2.70^b	69.33 ± 7.98^c	74.89 ± 1.38^c
	VS2	38.58 ± 2.32^a	51.10 ± 4.04^b	78.34 ± 3.38^c	70.52 ± 3.95^d
BOD_5	VS1	29.51 ± 9.45^a	35.48 ± 3.35^a	62.46 ± 4.53^b	69.08 ± 9.85^b
	VS2	46.25 ± 2.46^a	58.89 ± 9.95^b	79.27 ± 7.31^c	72.57 ± 4.81^c

a,b,c,d: means in the same row with different superscripts vary significantly ($p < 0.05$).
Symbol (±) is used for standard deviation. Values are mean of 8 measurements on different samples of waste.

Table 4 – Final pH and ammonia nitrogen concentration, mg l^{-1} in VS1 and VS2 experiments

Parameters	Experiment	Treatments			
		Z_0	Z_4	Z_8	Z_{12}
Total ammonia	VS1	330.5 ± 29.1^a	311.0 ± 29.8^{ab}	$297.0v39.4^{ab}$	259.8 ± 52.8^b
	VS2	356.0 ± 23.6^a	355.3 ± 18.8^a	327.0 ± 15.5^{ab}	290.8 ± 30.7^b
Free ammonia	VS1	15.32 ± 2.04^a	17.57 ± 1.55^{ab}	27.47 ± 4.08^c	21.35 ± 5.92^b
	VS2	17.49 ± 2.39^a	20.53 ± 0.72^a	28.88 ± 2.44^b	27.61 ± 3.51^b
pH	VS1	7.08 ± 0.02	7.18 ± 0.03	7.41 ± 0.03	7.35 ± 0.03
	VS2	7.11 ± 0.03	7.19 ± 0.02	7.39 ± 0.03	7.42 ± 0.02

a,b,c: means in the same row with different superscripts vary significantly ($p < 0.05$).
Symbol (±) is used for standard deviation. Values are mean of 8 measurements on different samples of waste.

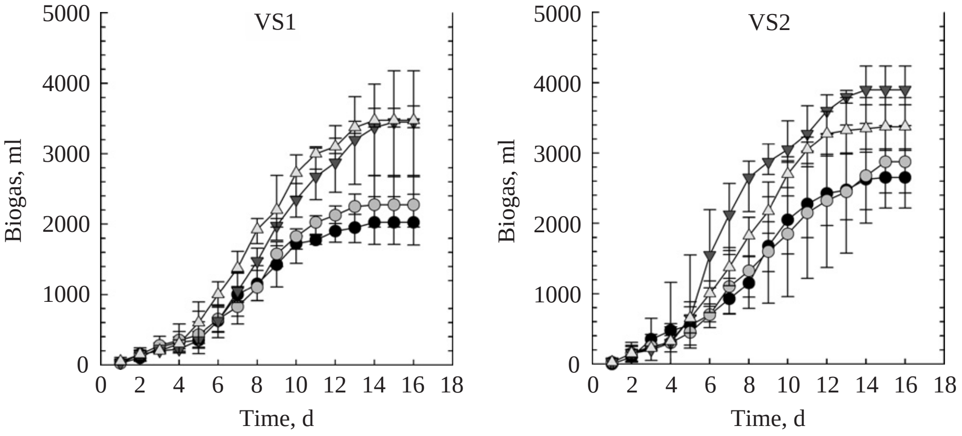

Fig. 1 – Volume of biogas accumulated with the time of digestion in VS1 and VS2 experiments. Doses of zeolite: —●—0 g l^{-1}; —○—4 g l^{-1}; —▼— 8 g l^{-1}; —△—12 g l^{-1}. The bars designate standard deviations.

78.34% in the VS2 experiment. A further increase in zeolite levels did not cause a significant increase of volatile solids removal in the VS1 experiment and caused a significant decrease of volatile solids removal in the VS2 experiment. However, the volatile solids removal in treatment Z_{12} was significantly higher than those in treatments Z_0 and Z_4.

Table 3 shows the biochemical oxygen demand (BOD_5) removal percentage achieved at the end of the batch process for the different doses studied in each replication. The removal efficiency was significantly higher in treatments with zeolite doses of 8 and 12 g l^{-1} compared to those with 4 g l^{-1} and without zeolite. Increasing zeolite to 8 g l^{-1} caused a significant removal of BOD_5, while further increase of zeolite dose did not affect BOD_5 removal.

The final concentrations of total and free ammonia nitrogen are shown in Table 4. Increasing the zeolite dose caused a slight decrease of the ammonia nitrogen concentration. Furthermore, as shown in Table 4, free ammonia concentrations were higher in treatments Z_8 and Z_{12} than those in treatments Z_0 and Z_4. However, with the addition of zeolite there was a decrease in the free ammonia concentration, because the value of the free ammonia concentration depends on the total ammonia concentration which was reduced.

In Fig. 1 the variation of the biogas volume accumulated with the digestion time in VS1 and VS2 experiments is shown. In all treatments, the process ceased in approximately 15 days. Biogas production varied from 0 to 900 ml day^{-1}. The results of methane production are summarised in Table 5. In the VS1 experiment the methane yields were 1629, 1836, 2637 and 2714 ml and in the VS2 experiment they were 2083, 2300, 3051 and 2627 ml for treatments Z_0, Z_4, Z_8 and Z_{12}, respectively. Methane production increased significantly with the increase of zeolite dose up to 8 g l^{-1} in both experiments. Further increases in the levels of zeolite in the VS1 experiment did not cause any increase in methane production. Further increasing the level of zeolite in VS2 experiment decreased methane production. The methane content in the biogas produced in all cases was around 78%. No significant differences in the methane content were observed among the treatments. The balance between VS reduction and methane production is illustrated in Fig. 2.

pH values in effluents varied from 7.06 to 7.45 as shown in Table 4. The values in treatments Z_8 and Z_{12} were Slightly higher than those in treatments Z_0 and Z_4. However, the values of pH were in the optimum range (6.8–7.5) for the growth of anaerobic bacteria (Lettinga & Haandel, 1993).

4. Discussion

Pig wastes contain a high concentration of ammonia; therefore, anaerobic digestion of pig waste, especially in the thermophilic range, has been characterised as difficult. The present study of thermophilic anaerobic digestion of pig wastes with different amounts of natural zeolites showed that the digestion performance was better in treatments with zeolite doses of 8 and 12 g l^{-1} (higher removal efficiency of BOD_5, volatile solids and more methane production) than that in treatments without zeolite and with zeolite dose of 4 g l^{-1}. This is mainly due to the ability of zeolite to reduce the concentration of NH_4^+ by ion exchange and therefore the concentration of free ammonia, because NH_4^+ and NH_3 are in equilibrium in the solution. In addition zeolite reduces directly the concentration of free ammonia in waste by adsorption on the active areas of the material (Milán *et al.*, 2001; Montalvo *et al.*, 2005; Tada *et al.*, 2005), thus

Table 5 – Total methane production, ml

	Treatments			
	Z_0	Z_4	Z_8	Z_{12}
VS1	1629.38 ± 263.78^a	1836.75 ± 270.16^a	2637.31 ± 337.60^b	2714.31 ± 118.55^b
VS2	2083.63 ± 208.68^a	2300.88 ± 252.06^a	3051.13 ± 197.10^b	2627.63 ± 269.47^c

a,b,c,d: means in the same row with different superscripts vary significantly ($p < 0.05$).
Symbol (±) is used for standard deviation. Values are mean of 8 measurements on different samples of biogas.

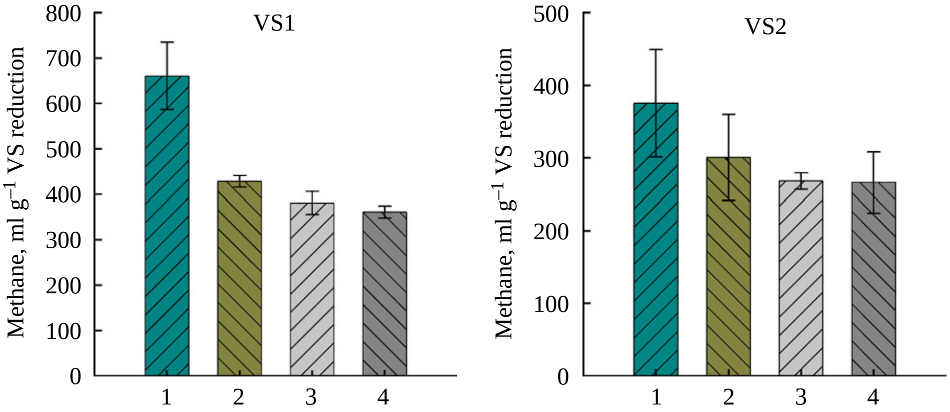

Fig. 2 – Effect of zeolite addition on methane production from pig waste after anaerobic digestion. Doses of zeolite: 1. 0 g l^{-1}; 2. 4 g l^{-1}; 3. 8 g l^{-1}; 4. 12 g l^{-1}. The bars designate standard deviations.

reducing the inhibitory effect of these compounds (Montalvo et al., 2006).

It has been reported, in previous studies, that the addition of clay minerals in thermophilic anaerobic digestion reduced the toxic effect of ammonia and so the methane production increased (Hansen et al., 1999; Angelidaki & Ahring, 1993). In these studies, ammonia concentrations were 2.5–5.2 g l^{-1}. In the present study, ammonia concentrations were 10–20 times lower than the above values. Nevertheless, the main result of both studies was that the addition of clay minerals has a positive effect on methane production. In both studies, the positive effect could not be entirely explained by the adsorption of ammonium ion. In the study with bentonite addition, the cation exchange capacity is too low (maximum ammonia exchange 130 mg [N] l^{-1}) to explain the methane enhancement, while the ammonia concentration did not decrease (Angelidaki & Ahring, 1993). In the present study, the ammonia concentration of ammonia is too low to cause these differences among the treatments in the anaerobic digestion. This could be explained by the fact that clay minerals could improve anaerobic digestion not only through the adsorption of ammonium ion but also through the influence of microbial and enzymatic transformations of a variety of other substances, as has been reported (Bremner, 1954). Another possible explanation could be that zeolite offers a high-capacity immobilisation matrix for microorganisms (Milán et al., 2001).

Furthermore, the results obtained from this research show that the pH values remain in any case within the optimum range for anaerobic digestion. This is in contrast to the previous research, where it was found that the addition of 10 g of zeolite per litre of waste increased the pH to 8.1. This fact was considered as the main reason for the process failure at these doses (Milán et al., 2001). In the present experiment, although the pH was higher in Z_8 and Z_{12} treatments than those in treatments Z_0 and Z_4, it was in the optimum range for anaerobic digestion. Also Tada et al. (2005) have found that the addition of zeolite in the anaerobic reactors did not affect the pH value. It is possible that the addition of zeolite affects not only the concentration of ammonia nitrogen but also the acidity (pH) in the reactors. Venglovsky et al. (2005) reported that zeolite addition affects pH regulation. Thus the toxic effect of ammonia, which is relevant to pH, could be reduced.

Variation among the treatments in the final ammonia nitrogen concentration was observed. This is mainly due to the different degrees of anaerobic decomposition among the treatments. It is well known that the organic nitrogen compounds are transformed to ammonia in anaerobic metabolism. Furthermore, ammonia concentration in Table 4 is a part of the total ammonia concentration because most of the non-ionized ammonia (NH_3) escapes from the solution according to Milán et al. (2001) and a part is removed by the zeolite.

The theoretical methane productivity in pig waste is 516 l kg^{-1} of volatile solids, while the ultimate methane yield in terms of volatile solids is 356 l kg^{-1} of volatile solids (Moller et al., 2004). In the VS1 experiment the methane yield in terms of volatile solids was 167.49, 188.85, 270.16 and 278.03 l kg^{-1} of volatile solids in treatments Z_0, Z_4, Z_8, and Z_{12} respectively, which means 47.05%, 53.05%, 75.80% and 78.10% of the ultimate methane yield, respectively. In the VS2 experiment the methane yield in terms of volatile solids was 143.24, 158.12, 209.75 and 180.64 l kg^{-1} of volatile solids in the treatments Z_0, Z_4, Z_8 and Z_{12}, respectively, which means 40.23%, 44.42%, 58.9% and 50.74% of the ultimate methane yield, respectively. In the experiment reported by Milán et al. (2001) in the mesophilic range, the maximum volume of methane accumulated in terms of volatile solids was about 161 l kg^{-1} of volatile solids and the concentration of zeolite in the waste was in the range 2–4 g l^{-1}.

In the VS2 experiment higher methane production, as shown in Table 5, was observed in treatment Z_8 whereas in treatment Z_{12} more zeolite was added. This could be explained according to Milán et al. (2001) that large amounts of zeolite could increase the apparent viscosity of the medium, which affects the transport of nutrients and metabolites and decelerates the anaerobic process.

In addition, as shown in Table 5, the methane production depends on the initial concentration of volatile solids; the concentration of total organic nitrogen was the same in VS1 and VS2 experiments, as shown in Table 2. As can be seen the methane production in the VS2 experiment was significantly higher in treatment Z_8 than that in treatment Z_{12}. In the VS2 experiment the initial concentration of volatile solids was higher than that in VS1 experiment and so probably the ratio C/N in the VS1 experiment was higher than that in the VS2 experiment. In the VS2 experiment, it is possible that the higher zeolite dose, which was used in treatment Z_{12} than that in treatment Z_8, affected the reduction of the amount of nitrogen to such an extent that the ratio C/N was increased above the optimum range. Thus, the production of methane was higher in treatment Z_8 than in treatment Z_{12}. The effect of zeolite on C/N ratio needs to be further investigated.

The zeolite dose which had the best results in anaerobic thermophilic digestion was 8 g l^{-1}. In previous research (Milán et al., 2001) the best results in mesophilic anaerobic digestion were obtained by zeolite doses between 2 and 4 g l^{-1}. The difference between these two studies may be due to the fact that different natural zeolites were used and that the current study was performed in the thermophilic range.

5. Conclusion

In this study eight reactors with different doses of natural zeolite were examined to evaluate biogas production from pig wastes in batch reactors under anaerobic thermophilic digestion. The main outcomes of this study are:

- The addition of 8 and 12 g $l^{-1}$of zeolite causes a significant increase in the methane production compared to those without zeolite, in the thermophilic anaerobic digestion of pig waste.
- The best environmental results could be obtained by the addition of natural zeolite, at doses between 8 and 12 g l^{-1}. This produces higher BOD_5 and volatile solids removal efficiency.
- The results appear to be caused by the addition of zeolite, which adsorbs ammonia, and thus affecting not only

the toxicity of ammonia and C/N proportion but also regulating the acidity (pH) of the pig wastes.

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