# Effect of natural and modified zeolite addition on anaerobic digestion of piggery waste

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**Abstract** The effect of natural and modified zeolites on the anaerobic degradation of acetate and methanol was evaluated by the determination of specific methane productivity (SMP) in batch minidigesters of 50 mL at doses of 0.01, 0.05 and 0.1 g of zeolite/g of VSS. The effects of the different zeolite concentrations were determined by the results of the SMP. A kinetic characterization with data of accumulated methane gas volume was also carried out. In the second phase of the study, the effects of natural and nickel zeolite concentrations were tested with piggery waste in laboratory scale digesters of 2.5 L operating at semi continuous mode, by increasing the organic load applied from 0.2 to 22.0 g TCOD/d corresponding to organic loading rates (OLR) of 0.1–8.8 g TCOD/l.d. A greater effect of modified zeolite on SMP was observed, with an increase of 8.5 times with magnesium zeolite, 4.4 times with cobalt zeolite and 2.8 times with nickel zeolite. Two phases were defined in the kinetic study and an increase of more than 2 times the apparent constant of digesters with modified zeolites was observed in the second phase when compared to unmodified natural zeolite. Modified natural zeolite addition to digesters can allow an increase in the potential biodegradability of piggery waste solid fraction and/or a considerable reduction of digestion volume.

**Keywords** Natural and modified zeolite; piggery waste; specific methane productivity (SMP)

## Introduction

One of the most important problems of pig breeding is the waste management which requires adequate treatment systems and disposal. The high strength and large volume of piggery waste causes nuisance effects on the environment. Among the different wastewater treatments, anaerobic digestion is considered to be the most suitable process given the high organic load and nutrient content of this waste. In addition, high organic and nutrient content wastes cause considerable environmental problems. Anaerobic processes are efficient in reducing the concentration of organic matter of piggery waste. The utilization of methane gas obtained in the process considerably reduces the treatment cost. Anaerobic treatment processes have also been applied to very strong soluble wastes (Llabrés and Mata-Alvarez, 1988; Hobson, 1992; Sánchez *et al*., 1995).

Clay minerals and other surface-active particles have been reported to influence microbial and enzymatic transformation of a variety of substances. In addition, zeolites have been found to be a successful support in mesophilic anaerobic digestion of different wastewaters, principally for: (1) the high capacity for immobilization of micro-organisms, (2) improving the ammonia/ammonium ion equilibrium and (3) availability of unbound ammonia in solution (Borja *et al*., 1993; Borja *et al*., 1996). Besides, the micronutrient addition is an important fact to obtain a greater efficiency in the anaerobic degradation of solid wastes (Ilangovan and Noyola, 1993; Sanchez, 1994).

Natural zeolite also has other uses in wastewater treatment technologies. Ionic exchange units using homoionic natural zeolite offer ammonium removals near 95%, operating in downflow mode (Milán *et al*., 1997). In addition, natural zeolite is an attractive solution as

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a filtering medium not only for effluents with low suspended organic content but also for effluents with high concentration of suspended matter (Reyes *et al.*, 1997; Milán *et al.*, 1999). In this work, the effect of modified and natural zeolite concentrations on anaerobic digestion of piggery waste was studied in a laboratory reactor operating at semi continuous mode.



## Material and methods

### Piggery waste

Piggery waste manure from a farm located near to the laboratory in Havana city (capacity of 4,500–5,000 heads) was used as inoculum. A manure-water dilution ratio 1:3 was prepared digested during 20 days. The characteristics of centrifuged sludge are shown in Table 1.

### Modified and natural zeolites

The natural zeolite with a particle size about 0.6–1.6 mm was obtained from Tasajera deposit, in Villa Clara Province (Cuba). Table 2 shows, its chemical and phase composition.

Heavy metals $Ni^{2+}$, $Co^{2+}$ and $Mg^{2+}$ were deposited on the natural zeolite surface, using heavy metals ionic exchanger and adsorption as reported in a previous paper. These modified zeolite samples were washed with deionized water (De las Pozas *et al.*, 1995). The relative exchange capacities of modified natural zeolites (based on the mg of deposited metal/g zeolite) were found to be: 2.60, 1.98 and 5.25 for nickel, cobalt and magnesium.

**Table 1** The characteristics of digested piggery manure used[a]

| Parameters (mg/l) | Averages |
|---|---|
| Total COD | 109,250 |
| TS | 57,795 |
| VTS | 43,795 |
| TSS | 44,457 |
| VSS | 36,496 |
| Total phosphate | 1,066 |
| N (Kjeldahl) | 1,178 |
| N ($NH_4^+$) | 1,864 |
| pH | 6.8 |

[a]Average of more than 50 samples with a variance coefficient lower than 5%. TS, total solids; VS, volatile solids; TSS, total suspended solids; VSS, volatile suspended solids

**Table 2** Chemical and phase composition of Tasajera natural zeolite

| Chemical composition | | Phase composition (%) | |
|---|---|---|---|
| $SiO_2$ | 58.05 | Clinoptilolite | 35 |
| $Al_2O_3$ | 11.94 | Mordenite | 15 |
| $Fe_2O_3$ | 4.36 | Montmorillonite | 30 |
| MgO | 0.77 | Others** | 20 |
| CaO | 5.94 | | |
| $Na_2O$ | 1.5 | | |
| $K_2O$ | 1.2 | | |
| IW* | 12.09 | | |
| Total | 95.32 | | |

*IW – Ignition Wastes. **Others – Calcite, Feldespate and Quartz

## Experimental procedure

### Catalytic or inhibitory effects of the different zeolite concentrations

The catalytic or inhibitory effect of natural and modified zeolites were determined by means of the method to assess the specific methane productivity of the sludge. All experiments were performed in triplicate with the addition of the following material concentrations: 0.01, 0.05 and 0.1 g of zeolite/g of VSS.

The experiments were carried out in minidigesters with a working volume of 50 mL. The digesters were hermetically closed with rubber caps provided with two holes, one for the introduction of substrate or for removing the digested and the other for the biogas outlet. Biogas produced was collected in gasometers by positive displacement of 15% Na(OH) solution, the volume of solution displaced was considered equivalent to the methane volume produced. The volume of methane produced from each digester was measured as a function of time, as described by Field *et al.*, 1988; Borja *et al.*, 1994). All runs were carried out using 35 mmol of acetate and methanol as substrates, at a temperature range between 30 ± 1°C.

### Semicontinuous experiments

The experiments were carried out in parallel in 2.5 L volume digesters. The inoculum was a 20% of the reactor effective volume. First, the digesters were filled with tap water until its effective capacity was reached. The natural and nickel modified zeolites were added when the biogas production was ceased. After this step organic loads from 0.20 to 22.0 g of TCOD/d of raw piggery waste with total COD of 26.8 g/l were successively applied. Total COD removal, alkalinity, acidity and pH values were determined at each organic load added. During the experiments the daily biogas production was measured. Metal concentration in the supernatant of digesters with modified natural zeolite was also determined. Experimental biogas production and the hydraulic retention time (HRT) were fitted to the Chen-Hashimoto model (Borja *et al.*, 1994).

### Determination of specific methane productivity and anaerobic microorganisms

Both determinations were undertaken for the zeolite concentrations with the highest specific methane productivity values. The anaerobic techniques used were essentially those of Hungate with a medium reported by Miller and Wollin (APHA, 1989). Anaerobic trophic groups were determined in these systems by the MPN technique, according to *Standard Methods for the Examination of Water and Wastewater* (1989).

## Results and discussion

### Catalytic or inhibitory effects

Table 3 presents the values of SMP in digesters with the different zeolites tested. The addition of natural zeolite produced a decrease of SMP compared to the control showing that natural zeolite addition affected the conversion of acetate and methanol to methane. A greater effect of modified natural zeolites on SMP was observed, compared to natural

**Table 3** Results of specific methane productivity expressed as g $COD_{CH4}$/g VSS.d, in the zeolite addition experiments

| g of zeo./g VSS | Natural zeo. | Nickel zeo. | Cobalt zeo. | Magnesium zeo. |
|---|---|---|---|---|
| Controls | 0.018 | 0.027 | 0.009 | 0.016 |
| 0.01 g/g | 0.011 | 0.078 | 0.014 | 0.028 |
| 0.05 g/g | 0.008 | 0.032 | 0.009 | 0.054 |
| 0.1 g/g | 0.007 | 0.029 | 0.040 | 0.135 |

zeolite. The best result was obtained with nickel modified zeolite at a dose of 0.01 g of zeolite/g of VSS. When the doses increased the SMP values decreased and approached the values observed in the control.

The values of SMP did not show a significant increase for doses of 0.01 and 0.05 g of cobalt zeolite/g of VSS, however a significant increase was obtained at 0.1 g of zeolite/g VSS. In the experiments with magnesium zeolite, a progressive increase of SMP with zeolite doses was observed, obtaining a maximum value of 0.135 g COD $CH_4$/g VSS at 0.1 g/g. This value was the maximum observed in all the experiments.

The major increase of SMP compared to the corresponding control values was 8.5 times that with magnesium zeolite, 2.8 times with nickel zeolite and 4.4 times with cobalt zeolite. These trace metal elements are required for some metabolic functions, also their high concentrations can provoke inhibition in metabolic routes. The addition of cobalt, nickel and molybdenum solutions also stimulates methanogenic bacteria.

Cobalt is necessary for corrinoids biosynthesis, being the central ion in vitamin $B_{12}$ derivates, which is involved in the transference of methyl groups in methanogenesis; it is present in both, methanotrophic and acetotrophic bacteria (Stupperich *et al.*, 1990; Jetten *et al.*, 1992). Its addition in solution as a trace element for the stimulation of full-scale digesters has been previously reported (Sánchez, 1994). Nickel is also important for methanogenic bacteria, and magnesium acts on some enzymatic carriers (Bitton, 1994).

In order to characterize the experiment kinetically, data of accumulated methane gas volume and digestion time were correlated by the following equation:

$$G = G_m\,[1 - \exp(-k_o t)] \qquad (1)$$

where: $G$ is the volume of methane gas accumulated at a given time $t$ (days); $G_m$ is the maximum volume accumulated at an infinite digestion time and also is the product of the initial substrate concentration and the methane yield coefficient, $k_o$ (days$^{-1}$) is an apparent kinetic constant that includes the biomass concentration. According to Eq. (1), methane production conforms to a first-order kinetic model (Borja *et al.*, 1996). Eq. (1) can be transformed into:

$$\mathrm{Ln}[G_m/G_m - G)] = k_0 t \qquad (2)$$

Indicating that a plot of $\mathrm{Ln}[G_m/G_m - G)]$ versus $t$ should give a straight line with a slope equal to $k_0$ with intercept zero if the model is applied to the experimental data.

Figure 1 shows the variation of the $\mathrm{Ln}[G_m/G_m - G)]$ values with time for the different experimental values for acetate substrate; both substrates acetate and methanol had similar behaviour. The value of $G_m$ has been considered to be equal to the volume of methane accumulated at the end of each experiment. Hence, it is possible to fit the experimental data to the proposed model, however the trend of curves shows a changed tendency with the addition of modified natural zeolites after a start-up period of experiment that lasted around 4 days in these systems. The parameter $k_o$ was calculated by a nonlinear regression program, for the two defined phases, phase I up to 4 day digestion time and phase II after this time.

Table 4 summarizes the $k_o$ values (days$^{-1}$) with 95% confidence limits obtained for modified and natural zeolite for both phases. In all cases, modified and natural zeolite systems, the $k_o$ values for phase I were between 0.06 and 0.11 d$^{-1}$ with acetate as substrate, while for methanol the values ranged between 0.19 and 0.25. In general, there was not a great difference among them. However, in the second phase a better kinetic behaviour in digesters with modified natural zeolite was observed, for both tested substrates. For most

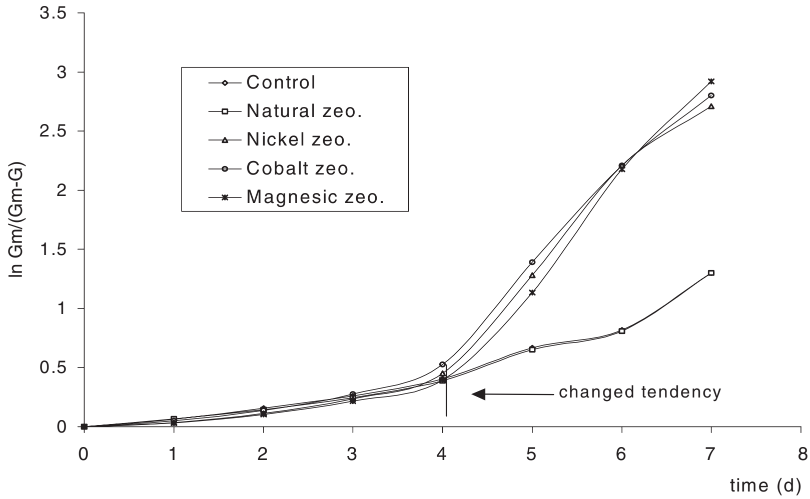


**Figure 1** The behaviour of zeolite systems with acetate as substrate

cases and both substrates an increase of apparent kinetic constant of more than two times when compared with that observed in control and natural zeolite was shown. The best kinetic behaviour was shown by magnesium modified zeolite.

The determination of biotic population was carried out for the system with the highest values of $k_o$: nickel modified zeolite and cobalt modified zeolite with methanol and magnesium modified zeolite with acetate as substrate.

A plot of the biotic population observed in the sludge before and after modified zeolite addition is shown in Figure 2. Comparing the microbial population at the end of the

**Table 4** Obtained values of $k_o$ ($d^{-1}$) to both substrates and phases

| Substrates | | Controls | Natural zeo. | Nickel zeo. | Cobalt zeo. | Magnesium zeo. |
|---|---|---|---|---|---|---|
| Acetate | Phase I | 0.11 ± 0.01 | 0.08 ± 0.01 | 0.06 ± 0.01 | 0.07 ± 0.01 | 0.07 ± 0.01 |
| | Phase II | 0.34 ± 0.08 | 0.35 ± 0.01 | 0.80 ± 0.04 | 0.76 ± 0.04 | 0.76 ± 0.04 |
| Methanol | Phase I | 0.20 ± 0.03 | 0.24 ± 0.02 | 0.25 ± 0.01 | 0.19 ± 0.04 | 0.25 ± 0.01 |
| | Phase II | 0.42 ± 0.07 | 0.41 ± 0.07 | 0.71 ± 0.03 | 0.82 ± 0.09 | 1.02 ± 0.01 |

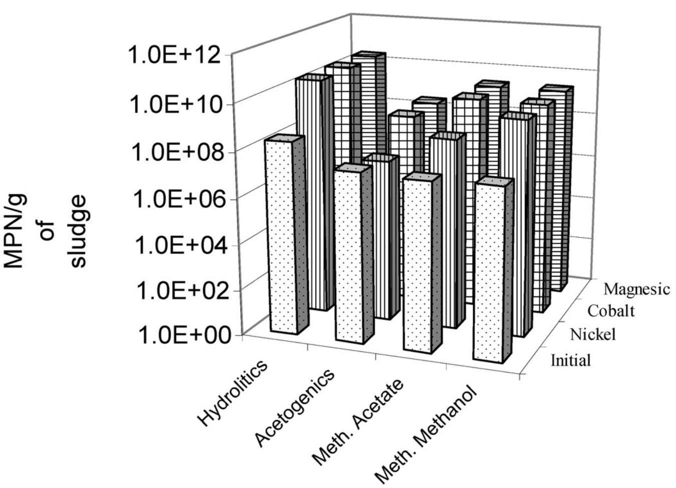


**Figure 2** The biotic population representation in the anaerobic sludge before and after modified zeolite addition

**Table 5** Average values of controlled parameters during all experimental period

| Parameters | Control | Natural zeolite | Nickel zeolite |
|---|---|---|---|
| pH | 7.7 ± 0.2 | 7.8 ± 0.3 | 7.8 ± 0.3 |
| Acidity (mg/L) | 124 ± 12 | 144 ± 14 | 114 ± 9 |
| Alkalinity (mg $H_2CO_3$/L) | 3067 ± 87 | 3413 ± 63 | 3555 ± 71 |
| Methane volume (ml/g of COD added) | 352 ± 66 | 447 ± 78 | 516 ± 73 |



experiment to the initial population of the inoculum, it was observed that MPN of hydrolytic bacteria increased by two logarithms with modified natural zeolite addition. Acetogenic bacteria increased by one logarithm for cobalt and magnesium zeolite but nickel zeolite did not stimulate these bacteria. The population of methanogenic (acetate) bacteria increased two logarithms compared to magnesium and cobalt zeolite and one logarithm by nickel zeolite. With regards to the population of methane (methanol) bacteria the population increased two logarithms for modified zeolites. Therefore the utilization of modified natural zeolite in anaerobic processes enhanced the growth of methanogenic bacteria.

### Semicontinuous experiments

Based on the previous results presented in Tables 3 and 4, a dose of 0.01 g /g of VSS was added of both natural and nickel modified zeolite. Table 5 presents the average values of controlled parameters during the whole experimental period.

The pH values were maintained near the upper limit of the optimum range. In general, a great difference among these parameters was not observed. However, taking into account the methane production and considering the digester behaviour as a completely mixed reactor operating in steady state, it is possible to obtain the maximum specific microbial growth rate by using the Chen-Hashimoto kinetic model (Eq. (3)) (Borja *et al.*, 1994).

$$HTR = 1/\mu_{max} + K/\mu_{max} \,.\, B/(B_0 - B) \quad (3)$$

where: HTR is the hydraulic retention time (days); $K$ is a kinetic constant; $\mu_{max}$ is the maximum specific microorganism growth rate (days$^{-1}$); $B$ is the volume of methane produced under STP conditions per gram of substrate added and $B_0$ is the volume of methane produced under STP conditions per gram of substrate added at infinite retention time.

In the steady without retention of microorganisms $\mu$ = 1/HRT. Then, the minimum retention time of microorganisms which avoids the washout of system is numerically equal to the reciprocal of the maximum growth rate (HRT = $1/\mu_{max}$). The $\mu_{max}$ values obtained ranged from 0.08 to 0.23 d$^{-1}$. In the control digester the value of $\mu_{max}$, was 0.10 ± 0.03 d$^{-1}$ . For natural zeolite and modified zeolites the values were 0.17 ± 0.03 d$^{-1}$ and 0.19 ± 0.04 d$^{-1}$ respectively.

## Conclusions

The utilization of zeolites modified with metals such as cobalt, nickel and magnesium was favorable to increase the methane production from acetate and methanol, the most important precursors of methanogenesis. The addition of modified zeolites determined an increase of the microbial growth not only for the methanogens but also for the hydrolytic bacteria. The kinetics constant for anaerobic degradation of acetate and methanol was increased by the addition of modified zeolites. The optimum doses for magnesium zeolite and cobalt modified zeolites were found to be 0.1 and 0.01 g/g VSS respectively.

The utilization of modified and natural zeolites in semicontinuous anaerobic digesters treating piggery waste demonstrated that modified zeolite contributed to increasing the process efficiency and to reducing the hydraulic retention time.


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## References


Bitton, G. (1994). *Wastewater Microbiology*. John Wiley & Sons, Inc.

Borja, R., Sánchez, E., Weiland, P. and Travieso, L. (1993) Effect of ionic exchanger addition on the anaerobic digestion of cow manure. *Environ. Technol.*, **14**, 891–896.

Borja, R., Sánchez, E., Weiland, P., Travieso, L. and Martin, A. (1994). Kinetics of anaerobic digestion of cow manure with biomass immobilized on zeolite. *Chem. Eng. J.*, **54**, B9–B14.

Borja, R., Sánchez, E. and Durán, M.M. (1996). Effect of the clay mineral zeolite on ammonia inhibition of anaerobic thermophilic reactors treating cattle manure. *J. Environ. Sci. Health*, A31(2), 479–500.

De las Pozas, C., Lopez, R., Díaz, C., Cora, M. and Roque, R. (1995). Location and reducibility of Ni- ions in HEU-Type zeolites. *J. Solid State Chem.*, 114, pp. 108–111.

Field, J., Sierra, R. and Lettinga, G. (1988). Ensayos anaerobios. In: *Proceedings of the "4th Seminario de Depuración Anaerobia de Aguas Residuales"*. Secretariado de Publicaciones, Universidad de Valladolid, Valladolid, Spain.

Hobson, P.N. (1992). Treatment of animal wastes and uses of treated residues. In: *Biotechnology for Pollution Control and Energy*. Proceeding of the Third Workshop of the Working Group on Biogas Production Technology Braunschweig, Germany, 5–7 May, pp. 48.

Ilangovan, K and Noyola, A. (1993) Availability of micronutrient during anaerobic digestion of molasses stillage using an UASB reactor. *Environ. Technol.*, **14**. pp 795–799.

Jetten, M., Stams, A. and Zehnder, A. (1992). Methanogenesis from acetate: a comparison of the acetate metabolism in Methanothrix soeningenu and Methanosarcina spp. *FEMS Microbiol. Rev.*, **88**, 181–198.

Llabrés, P. and Mata-Alvarez, J. (1988). Influence of temperature, buffer, composition and straw particle length on the anaerobic digestion of wheat straw-pig manure mixtures. *Res., Cons. and Recy.*, **1**, pp 27–37.

Milán, Z., Sánchez, E., Weiland, P., De las Pozas, C., Borja, R., Mayari, R. and Rovirosa, N. (1997). Ammonia removal from anaerobically treated piggery manure by ion exchange in columns packed with homoionic zeolite. *Chem. Eng. J.*, **66**, pp. 65–71.

Milán, Z., Sánchez, E., Borja, R., Ilangovan, K., Pellón, A., Rovirosa, N., Weiland, P. and Escobedo, R. (1999). Deep bed filtration of anaerobic cattle manure effluents with natural zeolite. *J. Environ. Sci. Health*, **B34**(2), 305–332.

Montalvo, S. and Sánchez, E. (1977). Estudio de la depuración anaeróbica de aguas de instalaciones porcinas. *Ing. Civil*, 6. No. 77.

Reyes, O., Sánchez, E., Pellón, A., Borja, R., Colmenarejo, M.F., Milán, Z. and Cruz, M. (1997). A comparative study of sand and natural zeolite as filtering media in tertiary treatment of wastewaters from tourist areas. *J. Environ. Sci. Health*, **A32**(6), pp. 1695–1709.

Sánchez, E. (1994). Effect of pyrite addition on anaerobic digestion. *Biores. Technol.*, 47, 2, 189–190.

Sánchez, E., Milán, Z., Borja, R. Weiland, P. and Rodriguez, X. (1995). Piggery waste treatment by anaerobic digestion and nutrient removal by ionic exchange. *Res., Cons. and Recy.*, **15**, pp. 235–244.

*Standard Methods for the Examination of Water and Wastewater* (1989). 17th ed. American Public Health Association, Washington DC, USA.

Stupperich, E., Eisinger, H. and Schuff, S. (1990). Corrinoids in anaerobic bacteria. *Ferms Microbiol. Rev.*, **87**, 355–360.