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Effect of particle size and doses of zeolite addition on anaerobic digestion processes of synthetic and piggery wastes

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Abstract

The contribution of natural zeolite to the enhancement of the anaerobic digestion processes of piggery waste and synthetic wastewater with similar strengths was studied. Natural zeolite of up to 1 mm particle size was used in batch experiments. The influence of the particle size of natural zeolite on the anaerobic digestion processes of these substrates was also studied. The anaerobic process was favoured by the addition of natural zeolite at doses of between 0.05 and 0.30 g/g of volatile suspended solids (VSS), the optimum value being 0.10 g/g VSS. A first-order kinetic model was used to fit the experimental data with a probability level of 95% ($P \leq 0.05$). Values of the kinetic constants were determined to be dependent on the zeolite doses, achieving a maximum value (0.218/d) at a dose of 0.10 g zeolite/g VSS and a minimum value (0.145/d) at a dose of 0.40 g zeolite/g VSS. Zeolite and sand as supports for the immobilization of microorganisms were compared using a synthetic substrate and significant differences in TCOD removal efficiencies and methane production were not found between these two supports. It was found that, under the experimental conditions evaluated, the main mechanism of anaerobic process enhancement, in the case of piggery waste, was the high capacity of zeolite for microorganisms immobilization while the capacity of this support for ammonia nitrogen reduction was not relevant. However, in the case of synthetic waste, both the capacity for microorganisms immobilization and for reducing the concentration of toxic nitrogen (NH_3) by the zeolite were relevant.

Keywords: Natural zeolite; Anaerobic processes; Ammonia nitrogen; Piggery waste; Synthetic wastewater.

1. Introduction

Anaerobic processes are efficient in reducing the concentration of organic matter of piggery waste with biogas production that can be used as the energy source [1–4]. Anaerobic treatment of piggery waste offers the advantage that the biogas produced contains 50–70% methane [4]. On the other hand, removal efficiencies between 75 and 85% in total chemical oxygen demand (TCOD) have been obtained using batch processes [4]. However, conventional digesters used in rural areas must be operated at retention times higher than 20 days in order to achieve adequate organic matter removal efficiencies and prevent the washout of microorganisms. The increase of wastewater anaerobic process efficiency by using natural and modified zeolites has been pointed out by several authors [5,6]. The adequate doses of natural zeolite have also been studied [7]. Doses of between 2 and 4 g/l of wastewater have been found to be the most adequate for stimulating anaerobic process of piggery waste [6]. These authors claim that zeolite addition improved the anaerobic digestion of piggery wastewater. Zeolite reduces the concentrations of ammonia and ammonium ion that are present in raw piggery wastewater and those produced during anaerobic degradation of proteins, amino acids and urea [7]. Zeolite is an efficient ion exchanger for removing ammonium ion from anaerobic effluents and municipal wastewater. Ion exchange processes using homoionic natural zeolite have shown ammonium removal from waters with efficiencies close to 95% [4,8–10]. Natural zeolite has

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also been used in combination with struvite crystallisation to recover 65–80% of the nitrogen as crystallized or adsorbed ammonium [10]. Besides, zeolite has a great capacity for adsorption of metals, such as copper, cadmium, lead and zinc, which can be toxic for microorganisms [11]. The decrease of ammonia nitrogen helps to reduce the concentration of ammonium because these species are in equilibrium. In addition, zeolite has a great capacity for adsorption and has been found to be useful as a microbial support both in aerobic and anaerobic processes of different wastewaters [12–18].

Taking into account the information obtained from the literature review, different experimental studies were carried out at laboratory-scale in order to evaluate the performance of anaerobic processes operating at high concentrations of total Kjeldahl nitrogen (TKN) and to establish the effect of different natural zeolite doses when zeolite is mixed with the inoculum in the anaerobic digestion processes of piggery and synthetic wastes.

2. Materials and methods

2.1. Piggery and synthetic wastes

The experiments were carried out with raw piggery waste obtained from a farm located near the laboratory (Havana city, Cuba). The characteristics and features of the piggery waste used are summarized in Table 1. Simultaneously, a synthetic waste with a similar strength to that contained in piggery waste was prepared by mixing urea, sucrose and sewage. The nitrogen concentration varied during the different experimental runs, reaching the possible toxic concentration values (>3000 mg/l) [14,16,20,24]. Domestic wastewater (sewage) was used as dilution water. The characteristics of this dilution water are shown in Table 2.

2.2. Natural zeolite and sand used

The natural zeolite used in the experiments was obtained from a deposit located in the Province of Villa Clara, Cuba.

Table 1
Characteristics of the piggery waste used

Parameters (units)	Average value[a]
Total COD (TCOD; g/l)	20.2
Total solids (TS; g/l)	14.1
Volatile solids (VS; g/l)	8.8
Total suspended solids (TSS; g/l)	7.9
Volatile suspended solids (VSS; g/l)	6.2
Total phosphorous (mg/l)	190
Organic nitrogen (mg/l)	590
Ammoniacal nitrogen (mg/l)	260
pH (–)	6.9

[a] Values are averages of 10 determinations on different lots of waste; there was virtually no variation (<4%) between analyses.

Table 2
Characteristics of the dilution water

Parameters[a] (units)	Average value
Total COD (TCOD; g/l)	0.94
Total solids (TS; g/l)	0.89
Volatile solids (VS; g/l)	0.50
Total suspended solids (TSS; g/l)	0.35
Volatile suspended solids (VSS; g/l)	0.29
Total phosphorous (mg/l)	10
Organic nitrogen (mg/l)	31
Ammoniacal nitrogen (mg/l)	10
pH (–)	8.0

[a] Values are averages of 10 determinations on different lots of waste; there was virtually no variation (<4%) between analyses.

Table 3 shows the characteristics and features of the zeolite used. The sand used in the experiments had a concentration of SiO_2 of 95%, a particle size of 1 mm and a density of 2.3 kg/l.

2.3. Equipment

Experiments were carried out in laboratory-scale digesters. Equipment included glass flasks of 2.5 l effective volume hermetically closed by rubber caps with two holes. One hole was used for the extraction of samples and raw waste addition to restore the original volume and the other for biogas outlet. Biogas produced in the process was bubbled through solutions of 15% (v:v) NaOH to remove CO_2 from biogas, and allowed the measurement of methane gas production. The volume of methane produced was determined indirectly from the amount of water displaced by the gas in 1 l Mariotte reservoirs fitted to the reactors. The accumulative volume of methane produced from each digester was measured every day as the equivalent volume of water displaced. The digesters were continuously mixed at 300 rpm by means of magnetic stirrers. The mixing was stopped for 1 h before sampling in order to take samples of the supernatants of digesters and to avoid the loss of biomass. The experiments lasted 40 days. During the operation time, the temperature varied in the range of 27–31 °C. Each experimental run was carried out by triplicate. As the

Table 3
Chemical and phase composition of the natural zeolite used

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[b]	20
CaO	5.94		
Na_2O	1.5		
K_2O	1.2		
IW[a]	12.09		
Total	95.85		

[a] IW, ignition wastes.
[b] Others, calcite, feldespate and quartz.

deviations between replicate samples were always <4%, mean values are reported in the corresponding tables and figures.

2.4. Inoculum

The inoculum of each digester was well digested piggery waste obtained from a laboratory-scale anaerobic batch digester after 50 days of digestion time. The characteristics of the inoculum used were: total chemical oxygen demand (TCOD): 60 g/l; total suspended solids (TSS): 67 g/l; volatile suspended solids (VSS): 40 g/l; pH: 7.2; total Kjeldahl nitrogen (TKN): 824 mg/l; total phosphorus (P): 710 mg/l. The specific methanogenic activity (SMA) of this sludge was: 0.09 g COD CH_4/g VSS d. The inoculum was mixed with the zeolite or sand before being introduced into the digesters.

2.5. Experimental procedure

Four sets of experiments were carried out in triplicate, as follows: Experiment 1 consisted of the evaluation of the effect of zeolite with heterogeneous particle size <1 mm on the digestion of piggery waste at doses of 0, 0.05, 0.10, 0.15, 0.20, 0.25,0.30 and 0.40 g zeolite/g of inoculum (VSS); Experiment 2 consisted of the comparison of anaerobic digestion of synthetic waste using zeolite of heterogeneous particle size <1 mm added at a dose of 0.1 g/g of inoculum (VSS), sand with a similar dose and size, and a control. In this experiment, the synthetic waste had a concentration of TKN of 2.5 g/l; Experiment 3 consisted of the evaluation of the effect of TKN concentration. Therefore, a synthetic waste with a concentration of TKN in the range of 2.50–3.25 g/l was used as substrate and zeolite of heterogeneous particle size <1 mm and dose of 0.1 g zeolite/g inoculum (VSS) was employed. Finally, Experiment 4 consisted of the evaluation of a particle size of zeolite in ranges from 0.07 to 0.5 mm and 0.5 to 1 mm and doses from 0.05 to 0.20 g zeolite/g inoculum (VSS) on the anaerobic digestion of a synthetic waste with a TKN concentration of 3.0 g/l. In all experiments, the digesters were inoculated in the same way, with 250 ml of well digested sludge and the corresponding amounts of zeolite or sand. Control digesters were only inoculated with digested sludge. Once the inoculum was added to the digesters, their volumes were completed with the addition of 2.25 l of waste.

2.6. Analyses

The following parameters were determined in the experiments: total COD (TCOD), total suspended solids (TSS), volatile suspended solids (VSS), total Kjeldahl nitrogen (TKN), total ammonia nitrogen ($N-NH_X$), total phosphorus (P) and pH. These analyses were carried out according to Standard Methods for the Examination of Water and Wastewater [21].

3. Results and discussion

3.1. Experiment 1

This set of experiments evaluated the influence of different zeolite doses on the anaerobic digestion of piggery waste. Fig. 1 shows the variation of the values of TCOD of the supernatants with digestion time for the different zeolite doses studied. After the 35th day, the concentration of TCOD remained practically constant indicating that anaerobic digestion practically ceased. Values of TCOD at the end of the experiment at zeolite doses in the range of 0.05–0.30 g zeolite/g VSS were significantly lower than those observed in the control. Therefore, zeolite addition had a positive effect on the anaerobic digestion of this waste as has been previously reported [6,7]. It was observed that the minimum value of final TCOD of the effluents corresponded to a dose of 0.10 g zeolite/g VSS. A further increase of zeolite doses caused a significant decrease in the organic matter removal of the digestion process. At a dose of 0.40 g zeolite/g VSS, the TCOD at the end of the experiment was higher than in the control reactor showing that zeolite affected the process. The increase of the zeolite doses per gram of inoculum (VSS) used may have affected the mass transfer of organic matter, either nutrients and metabolites, in the vicinity of zeolite particles and the microorganisms associated. In addition, high amounts of zeolite may be toxic due to the accumulation of heavy metals [6,7,22].

In order to evaluate kinetically the effect of the addition of different doses of zeolite on the anaerobic digestion of piggery waste, the following first-order kinetic model for TCOD degradation was used [7,23]:

$$\frac{S}{S_0} = \exp - \left[k_1 t_d \left(\frac{X_0}{S_0} \right) \right] \tag{1}$$

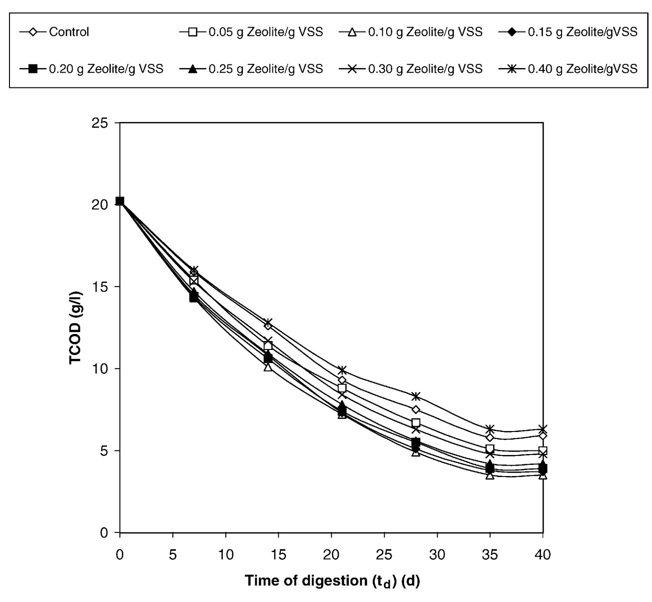

Fig. 1. Variation of the TCOD with digestion time at different doses of zeolite in the anaerobic digestion of piggery waste.

where S is the concentration of organic matter (g TCOD/l) at any digestion time, S_0 the initial substrate concentration (g TCOD/l), k_1 a first-order kinetic constant (g TCOD/g VSS d), t_d the time of digestion (d) and X_0 is the initial concentration of microorganisms (g VSS/l). The value of the quotient X_0/S_0 was determined to be 0.22 g VSS/g TCOD at the beginning of the experiments. Taking into account the constant value of this quotient (X_0/S_0), the value of k_1 may be determined for each zeolite dosage. Therefore, the product $k_1(X_0/S_0)$ is also a constant, known as apparent kinetic constant and denoted as k_1' (1/d). Therefore, Eq. (1) can be simplified and rewritten as follows:

$$\frac{S}{S_0} = \exp - (k_1' t_d) \quad (2)$$

The corresponding value of k_1' at different doses of zeolite may be determined by linearization of Eq. (2), as follows:

$$-\ln\left(\frac{S}{S_0}\right) = \}k_1' t_d \quad (3)$$

According to Eq. (3) a plot of $-\ln(S/S_0)$ versus t_d should give a straight line of slope equal to k_1' and intercept equal to zero. By fitting the experimental data to a linear function, using the least squares method, the slopes of the different lines obtained were calculated, which coincided with the k_1' values, from which the corresponding k_1 values were also calculated. A group of straight lines with high values of the regression coefficients were obtained showing that slope values (k_1') were dependent on the zeolite doses used. Table 4 shows the values of k_1', k_1 and the corresponding regression coefficients obtained for the different doses of zeolite used and for the control. Compared to the control, the values of both constants (k_1' and k_1) increased when the doses of zeolite increased up to 0.10 g zeolite/g VSS. At higher doses, the values of the kinetic constants decreased, achieving the minimum value for a dose of 0.40 g zeolite/g VSS. Therefore, the kinetic process was increased in a range of zeolite doses of between 0.05 and 0.10 g zeolite/g VSS. This enhancement effect was reduced when the doses of zeolite increased up to a value of 0.30 g Zeolite/g VSS. However, for a dose of 0.40 g zeolite/g VSS a significant inhibition was observed. For this dose, the values of k_1' and k_1 were lower than those observed for the control. This could be explained by the considerable increase of total solids concentration due to the addition of a high zeolite dose, which provokes simultaneously a reduction of the free available water affecting the transport of nutrients and metabolites in the vicinity of the zeolite particles and microorganisms associated [6,7]. Therefore, large amounts of zeolite could increase the apparent viscosity of the medium, thereby hindering mass transfer between the substrate and microorganisms responsible for the process and decelerating the digestion process. The values of the apparent kinetic constants obtained in this study were slightly higher than those obtained when zeolite addition was carried out on the mixture of inoculum and substrate [7]. Fig. 2 shows the variation of the volume of methane gas accumulated with the time of digestion for the different zeolite doses studied. As can be seen, typical curves of similar shape were obtained with slopes depending on the zeolite dose used. The maximum values for the slope and methane production (G_M) were obtained at a zeolite dose of 0.10 g zeolite/g VSS and the minimum value at a dose of 0.40 g zeolite/g VSS.

Table 4
Values of the kinetic constants k_1' and k_1 determined according to the linearized model represented by Eq. (3) for the different doses of zeolite used

Zeolite doses (g zeolite/g VSS)	k_1' (1/d)	R^2	k_1 (g TCOD/g VSS d)
0 (Control)	0.034	0.99	0.155
0.05	0.038	0.99	0.172
0.10	0.048	0.99	0.218
0.15	0.046	0.99	0.209
0.20	0.045	0.99	0.205
0.25	0.043	0.99	0.196
0.30	0.039	0.98	0.177
0.40	0.032	0.99	0.145

The variance coefficients of both kinetic constants were lower than 5% in all cases.

3.2. Experiment 2

In this group of experiments, zeolite and sand at similar doses (0.10 g/g VSS) and size (lower than 1 mm) were comparatively evaluated as supports using a synthetic substrate containing a TKN concentration of 2.5 g/l. Table 5 summarizes the results obtained with both materials compared with those obtained in a control digester. As can be

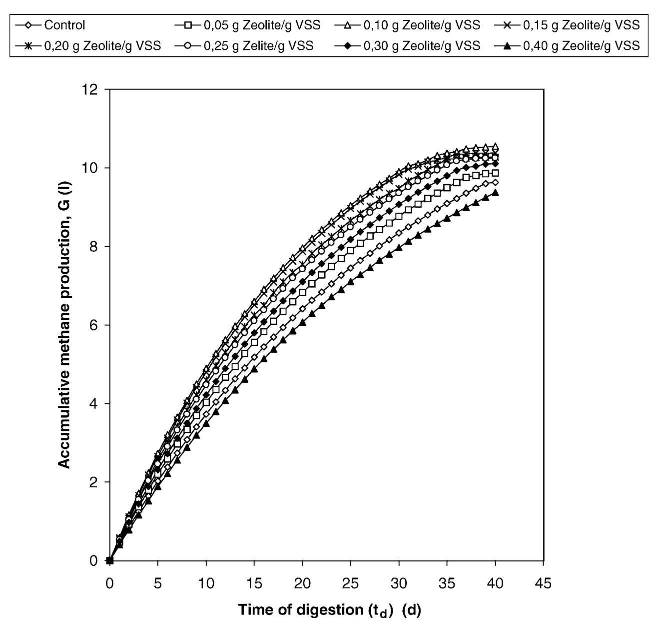

Fig. 2. Variation of the accumulative methane production with digestion time at different doses of zeolite in the anaerobic digestion of piggery waste.

Table 5
Comparison between the results obtained in the anaerobic digestion of a synthetic substrate using a control, zeolite and sand addition at doses of 0.1 g/g VSS

Parameter[a]	Initial value	Control		Zeolite		Sand	
		Final value	Removal (%)	Final value	Removal (%)	Final value	Removal (%)
TCOD (g/l)	20.00	5.40	73.0	2.81	86.0	2.75	86.2
TKN (g/l)	2.50	2.46	1.4	2.44	2.4	2.48	0.8
$N\text{-}NH_X$ (g/l)	0.10	2.36	–	2.24	–	2.24	–
pH	7.4	8.2	–	8.2	–	8.2	–
G_M (l)		9.85	–	10.84	–	10.86	–
Y_M (l/g TCOD)		0.30		0.28		0.27	

[a] Values are averages of three determinations on samples taken after 40 days of digestion. The differences between the observed values were <4% in all cases. $N\text{-}NH_X$: total ammonia concentration (g/l); G_M: maximum volume of methane accumulated (l); Y_M: methane yield coefficient (l CH_4/g TCOD).

seen, significant differences between the results obtained with zeolite and sand were not observed. However, in the case of the control digester, TCOD removal was always lower than observed in the digesters containing these two support materials. The final concentration of TCOD in the control was nearly double that obtained in the digesters with these materials. Comparing both materials, the TCOD removal efficiency values were very similar, and these values were significantly higher than those obtained in the control. The concentration of total ammonia nitrogen for the control digester was 2.36 g/l, while for the immobilized biomass reactors, the final concentration was lower. Besides, the maximum methane gas production was significantly higher in the digesters with immobilized biomass, although methane yield (Y_M) was slightly higher in the control reactor than in reactors with supported biomass. This may well be due to the fact that the use of support was favourable for microbial growth and in these cases more organic matter was consumed for cellular synthesis [16,19,24,25]. Due to the low doses of zeolite used no influence in the reduction of ammonia nitrogen was observed. As it is reported in the literature, the capacity of ammonia nitrogen exchange for natural zeolite is in a range of 5–14 mg NH_4^+/g zeolite [7,8,11,12,16]. Therefore, the amount of ammonia nitrogen removed from solution by ion exchange by zeolite was limited in this study to values of around 2–6 mg/l. Hence, the capacity for biomass immobilization was the main mechanism that determined the higher performance of zeolite and sand compared with the control.

3.3. Experiment 3

In this experiment, the influence of different initial concentrations of TKN in digesters with biomass immobilized on zeolite and in a control digester using a synthetic substrate as influent was studied. Table 6 summarizes the main results obtained. As can be seen, the values of the TCOD removal and maximum accumulative methane production were higher in the digester with immobilized biomass than in the control. Fig. 3 illustrates the variation of TCOD removals with the initial TKN concentration in the digester with zeolite and control. It was observed that an increase in the initial TKN concentration had no significant influence on the TCOD removal, except at a concentration of 3.25 g/l, where a decrease was observed. During the experiment, TCOD removal was always higher in the immobilized biomass reactor than in the control. However, the response of both reactors to an increase in the TKN concentration was very similar. Fig. 4 shows the variation of the concentrations of (TKN) and total ammonia nitrogen ($N\text{-}NH_X$) at the end of the experiment with the initial concentration of TKN ($(TKN)_0$). An increase in the $(TKN)_0$ caused an increase of both (TKN) and $N\text{-}NH_X$ at the end of the experiment for both zeolite and control digesters. The concentration of total ammonia nitrogen in the supernatant of the digester with zeolite addition was always lower compared with that observed in the control. Zeolite may contribute to reducing the concentration of ammonia by ion exchange in synthetic waste due to the lower concentration of suspended solids present in this substrate when compared with piggery waste. Therefore, the presence of zeolite helped reduce the concentration of both free ammonia (NH_3) and ammonium ion (NH_4^+) in the supernatant of the digestion process, thus reducing the inhibitory effect of these compounds [7,16]. The addition of zeolite could reduce both NH_4^+, by ion

Table 6
Effect of the initial concentration of total kjeldahl nitrogen $(TKN)_0$, on the anaerobic digestion of a synthetic substrate in digesters with biomass immobilized on zeolite and in a control digester

Parameter	Zeolite (0.10 g zeolite/g VSS)				Control			
$(TKN)_0$[a] (g/l)	2.50	2.75	3.00	3.25	2.50	2.75	3.00	3.25
$(N\text{-}NH_X)_0$[a] (g/l)	0.10	0.10	0.11	0.11	0.10	0.10	0.11	0.11
$(pH)_0$[a]	7.4	7.5	7.8	7.7	7.5	7.5	7.8	7.7
TCOD removal (%)	86.0	88.3	89.1	83.4	73.0	73.0	76.2	70.1
$(pH)_F$	8.2	8.2	8.3	8.4	8.2	8.2	8.3	8.4
$(TKN)_F$ (g/l)	2.36	2.57	2.62	2.88	2.56	2.57	2.62	3.01
$(N\text{-}NH_X)_F$ (g/l)	2.24	2.46	2.50	2.80	2.46	2.46	2.50	2.90
NH_3[b] (g/l)	0.22	0.24	0.30	0.41	0.24	0.24	0.30	0.43
G_M (l)	10.84	11.09	11.31	10.35	9.85	9.71	10.15	9.33

Values are averages of three determinations on samples taken after 40 days of digestion. The differences between the observed values were <4% in all cases. The influent TCOD concentration remained constant in the value of 20.0 g/l.

[a] The subscripts "0" and "F" represent the respective parameter values in the influent and effluent of the anaerobic processes.

[b] Values obtained from Eq. (5).

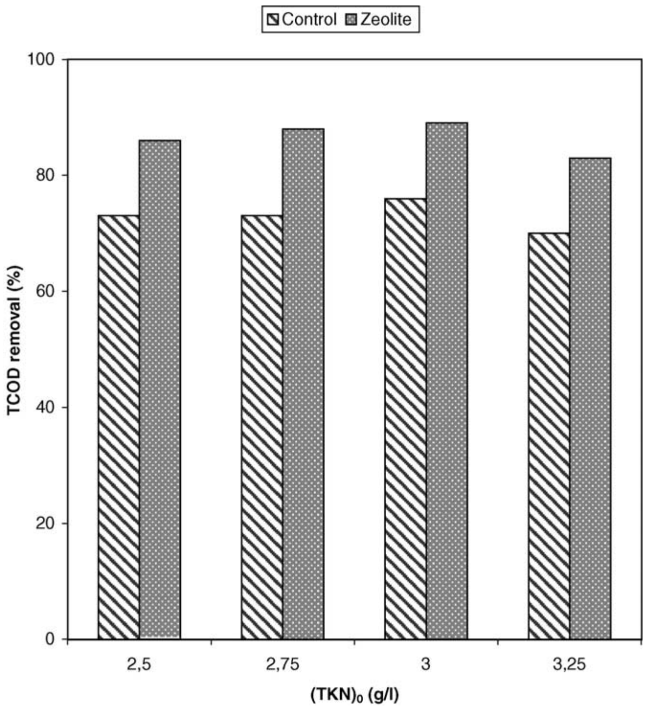

Fig. 3. Effect of the initial concentration of TKN on the TCOD removal efficiency in the anaerobic digestion of the synthetic waste.

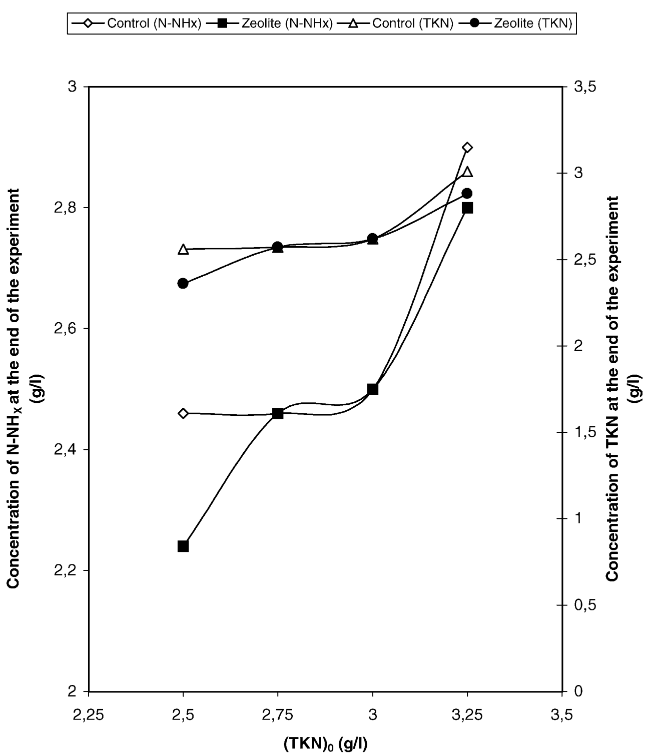

Fig. 4. Effect of the initial concentration of TKN on the concentrations of TKN and total ammonia nitrogen (N-NH_X) at the end of the experiments in the anaerobic digestion of synthetic waste.

exchange delivering Mg^{2+}, Ca^{2+} and Na^+ to the digester liquor, and NH_3, by adsorption of this specie on the active areas of the material; the two mechanisms were favourable for the anaerobic digestion of this waste [7,16,26–28].

The concentration of NH_3 balances out with the concentration of NH_4^+ by the following equation:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (4)$$

The equilibrium equation for this reaction is as follows:

$$K_E = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad (5)$$

where K_E is the equilibrium constant, with a value of 1.8×10^{-5}, $[NH_4^+]$ the concentration of ammonium ion (mol/l), $[OH^-]$ the concentration of hydroxyls (mol/l) and $[NH_3]$ the concentration of ammonia (mol/l). According to Eq. (5), the concentration of NH_3 rises with the increase of ammonium cation concentration and with the pH. For values of $(N\text{-}NH_X)_F$, and $(pH)_F$ at the end of the experiment given in Table 6 and using Eq. (5), the theoretical values of (NH_3) were calculated. In this way, the concentration of NH_3 in the digester with zeolite addition ranged from 0.22 to 0.41 g/l while in the control it ranged from 0.24 to 0.43 g/l. In both cases, the concentration of NH_3 was higher than that reported to be toxic for anaerobic processes. However, in the case of the digester with zeolite addition, the minimum and maximum values were always lower than those observed in the control. These results demonstrate that zeolite addition can reduce the concentration of this inhibitory compound in the case of a synthetic waste. However, this effect is irrelevant when piggery waste is used as substrate.

3.4. Experiment 4

Finally, the aim of this experiment was to study the influence of the particle size and doses of zeolite on the TCOD removal and methane production in the anaerobic digestion process of a synthetic substrate. As can be seen in Table 7, TCOD removal and accumulative methane produc-

Table 7
Effect of the particle size and doses of zeolite on the TCOD removal and maximum accumulative methane production (G_M) of the anaerobic digestion process of a synthetic substrate containing a TCOD concentration of 20.0 g/l and a TKN concentration of 3000 mg/l

Zeolite doses (g/g VSS)	Particle size (mm)	TCOD removal (%)	G_M (l)
Control	–	65.3	8.82
0.05	0.07–0.50	76.4	10.25
0.05	0.50–1.00	89.3	12.03
0.10	0.07–0.50	79.8	10.64
0.10	0.50–1.00	94.2	12.45
0.20	0.07–0.50	73.7	9.95
0.20	0.50–1.00	80.7	10.73

Values are averages of three determinations on samples taken after 40 days of digestion. The differences between the observed values were <4% in all cases.

tion values were lower in the control digester than in the digesters with zeolite addition. Besides, higher removal values were obtained for a particle size in the range of 0.50–1.00 mm than for the range of 0.07–0.50 mm. This is probably because microorganisms attachment was more favourable for larger particle size and consequently the ion exchange achieved for this particle size was optimum [26,27]. In this set of experiments, the maximum removal was achieved at a dose of 0.10 g zeolite/g VSS, regardless of the particle size used. It was also observed that TCOD removal values were higher for synthetic waste than for piggery waste, as was seen in Experiments 2 and 3.

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