



# Composting domestic sewage sludge with natural zeolites in a rotary drum reactor

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## ABSTRACT

This work aimed the influence of zeolites addition on a sludge-straw composting process using a pilot-scale rotary drum reactor. The type and concentration of three commercial natural zeolites were considered: a mordenite and two clinoptilolites (*Klinolith* and *Zeocat*). Mordenite caused the greatest carbon removal (58%), while the clinoptilolites halved losses of ammonium. All zeolites removed 100% of Ni, Cr, Pb, and significant amounts (more than 60%) of Cu, Zn and Hg. *Zeocat* displayed the greatest retention of ammonium and metals, and retention efficiencies increased as *Zeocat* concentration increased. The addition of 10% *Zeocat* produced compost compliant with Spanish regulations. Zeolites were separated from the final compost, and leaching studies suggested that zeolites leachates contained very low metals concentrations (<1 mg/kg). Thus, the final compost could be applied directly to soil, or metal-polluted zeolites could be separated from the compost prior to application. The different options have been discussed.

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## 1. Introduction

The elimination of biological sewage sludge from wastewater treatment plants is a significant problem in European cities due to the large amount of wastewater. More than 10 million tones of sewage sludge per year (expressed as dry matter) are currently produced in the 27 EU States, and 4 million tones are applied to agricultural land (Milieu Ltd., 2008).

Currently, composting is one of the most common treatments of sewage sludge. In this process, organic matter is transformed into compost, which is a stable, pathogen-free product that is often used as a soil additive due to the agronomic value of the material. However, due to the presence of toxic compounds such as heavy metals (Mosquera-Losada et al., 2010), applications of compost to agricultural land are limited. Environmental legislation limits the concentration of heavy metals in sewage sludge for use in agriculture (CEC, 1986), such that heavy metals must be removed from sewage. After the composting process, the concentration of heavy metals in the sludge is still relatively high (Smith, 2009), which prevents compliance with the provisions of law, and the compost cannot be applied to the soil.

Another disadvantage of sludge composting is the release of ammonia due to the decomposition of nitrogenous material (proteins and amino acids). The emission of ammonia frequently occurs during the thermophilic stage of composting. At low initial C/N

ratios, ammonia emissions from sewage sludge tend to be high (De Guardia et al., 2008; Liang et al., 2006). Losses of ammonia must be controlled during composting to enhance the agronomic value of the compost and reduce atmospheric pollution.

The addition of zeolites into sewage sludge may provide several benefits during the composting process. Zeolites are hydrated crystalline aluminosilicate minerals that occur as three-dimensional frameworks of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. Zeolites possess an open reticular structure formed by cavities with molecular dimensions between 3 and 10 Å. Zeolites have many industrial and environmental applications, and have been used in adsorption and ion exchange processes. The porous micro-structure of zeolites leads to the adsorption of a variety of elements, and the diameter of the input channels allows zeolites to act as a molecular sieve (Mumpton, 1999). Natural zeolites have been shown to effectively remove lead, cadmium, thorium, lead, zinc, manganese and ammonia from polluted effluents (Alvarez-Ayuso et al., 2003; Erdem et al., 2004; Ghaly and Verma, 2008). Previous studies have shown that the addition of natural zeolites to solid materials such as sewage sludge or compost leads to a significant reduction in the concentration of heavy metals (Kosobucki et al., 2008; Sprynskyy, 2009; Turan, 2008).

Taking into account the above described potential use of zeolites, the applicability of zeolites to the retention of metals and ammonia during the sludge composting process has been investigated (Stylianou et al., 2008; Turan and Ergun, 2007, 2008; Venglovsky et al., 2005; Zorpas et al., 2000a,b, 2002, 2003; Zorpas and Loizidou, 2008). Several effects of zeolites have been

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hypothesized. Zeolites could be used as bulking agents increasing the sludge porosity (Stylianou et al., 2008; Turan and Ergun, 2008), influencing also temperature and moisture. Zeolites take up heavy metals during composting (Zorpas et al., 2000a, 2002) and increase Na and K concentrations in compost through ion exchange (Malamis et al., 2010). Finally, ammonia emissions could be reduced by using these additives (Turan and Ergun, 2007). No studies have been found regarding the comparison of different kinds of zeolite.

The aim of this work was to study the effect of the addition of natural zeolites on the composting of domestic sewage sludge. To this end, a pilot-scale rotary drum composting reactor was constructed, and sewage sludge was composted under a variety of different conditions. The type and concentration of zeolite added to the sludge was varied, and the effects on metal and ammonia retention, temperature, moisture content and the evolution of volatile solids were analysed. After the composting process, the zeolites were removed from the compost, and leaching tests were conducted to estimate the leachability of the metals from the zeolites.

## 2. Methods

### 2.1. Experimental setup

Composting processes were carried out in a pilot-scale closed rotary drum reactor with forced aeration (Fig. 1). The composting reactor was adapted from the commercial model *Multicomp 3* (Kollvik Recycling S.L., Irún, Spain), and additional control and analysis systems were installed. The reactor had a capacity of 100 L and was operated as a fixed-bed batch reactor. A rotary system was employed to turn the reactor, and a motor was connected to the rotation axis. The approximate length and diameter of the drum were 0.7 m and 0.5 m, respectively. The drum was made of polypropylene and was coated with a thermal insulating material. A valve was used to pump atmospheric air into the reactor and a rotameter was used to control the airflow. To prevent the sludge from drying out and to achieve the desired temperature, the air was moistened, heated and uniformly distributed at the bottom of the reactor. A thermocouple in the reactor indicated the temperature of the biowaste, and a temperature controller was used to

turn off the heat when the temperature of the biowaste was greater than 65 °C. Leachate that accumulated at the bottom of the reactor was reintroduced into the solid waste when the reactor was rotated. Moreover, rotation helped to maintain the desired moisture level inside the reactor. The reactor was turned every day during the first two weeks of the process and was turned one or two times a week as the process progressed. The thermocouple and the air inlet and outlet pipes were disconnected when the reactor was turned. To evaluate the concentration of O<sub>2</sub>, CO<sub>2</sub> and NH<sub>3</sub> in the reactor, and to obtain a mass balance, the outlet air was analysed via an online gas analyser (Hidrolab model, Albacete, Spain).

### 2.2. Materials

Anaerobically-digested sewage sludge (DSS) from a domestic wastewater treatment plant in Ciudad Real (Spain) was used in this study. Barley straw (BS) was used as an amendment and was obtained from a university experimental farm ("Dehesa de Galiana", Ciudad Real, Spain). Straw was milled with an IKA® A 11 basic mill to achieve a particle size of approximately 2–3 mm. Table 1 provides a detailed description of the materials.

Three different natural zeolites were used in the composting experiments, including mordenite, (Mordenite 4/20), a natural zeolite from the south of Spain (marketed by BENESA, Spain), clinoptilolite, (*Klinolith*), a natural zeolite from eastern Europe (marketed in Spain by SOLINTECO), and another type of natural clinoptilolite (clinoptilolite E568, *Zeocat*, marketed by ZEOCAT, Barcelona, Spain). All of the zeolites possessed a particle size between 5–6 mm and a pore size less than 2 nm. Table 2 shows the basic characteristics of the zeolites (the data was provided by the manufacturers or distributors).

### 2.3. Composting experiments

A homogeneous mixture of digested sewage sludge and barley straw was prepared to obtain moisture content between 65–80% and a C/N ratio of 29. Depending on the experiment, different types and concentrations of natural zeolite were added; however, the average particle size of the materials remained constant (5–6 mm). The reactor was completely filled with sludge, straw

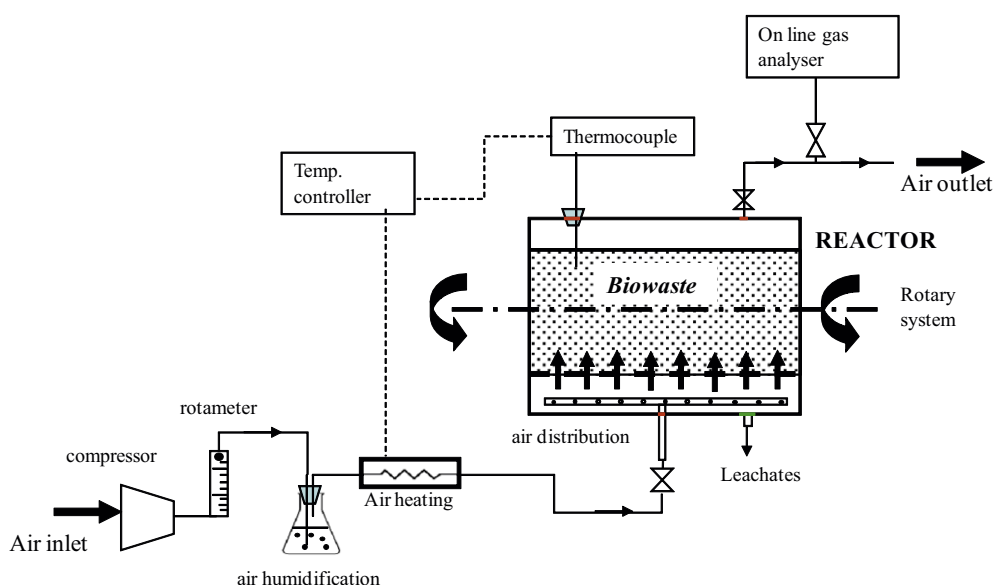


Fig. 1. Schematic depiction of the pilot scale composting system.

**Table 1**

Characteristics of the materials used in the experiments (dry weight).

Parameter	Digested sewage sludge (DSS)		Barley straw (BS)	
	Mean	SD	Mean	SD
Moisture (%) <sup>a</sup>	78.8	5.6	8.4	1.5
TC (%)	26.3	3.7	61.0	2.7
TN (%)	2.4	0.4	1.1	0.3
C/N ratio	10.9	–	55.5	–
pH <sup>a</sup>	8.2	0.2	8.3	0.4
TS (%) <sup>a</sup>	21.2	5.6	91.6	1.5
VS (%)	81.0	2.8	88.7	9.9
Cr (mg kg <sup>-1</sup> )	18.9	5.1	nd	–
Ni (mg kg <sup>-1</sup> )	11.4	6.6	nd	–
Pb (mg kg <sup>-1</sup> )	83.2	33.0	nd	–
Hg (mg kg <sup>-1</sup> )	1.56	0.72	nd	–
Zn (mg kg <sup>-1</sup> )	723.4	208.7	nd	–
Cu (mg kg <sup>-1</sup> )	267.9	114.3	nd	–
Cd (mg kg <sup>-1</sup> )	nd	–	nd	–

SD: Standard Deviation ( $n = 10$ ); TC: Total Carbon; TN: Total Nitrogen; VS: Volatile Solids; nd: not detected.<sup>a</sup> Wet basis.**Table 2**

Characteristics of the Zeolites.

Type of Zeolite	Acidity (mmol NH <sub>3</sub> g <sup>-1</sup> )	Exchange Capacity (meq NH <sub>4</sub> <sup>+</sup> g <sup>-1</sup> )	Composition (%) SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	
Mordenite 4/20 (Mordenite)	0.588	45.0·10 <sup>-3</sup>	71.0	11.0
Klinolith (Clinoptilolite)	0.976	50.8·10 <sup>-3</sup>	65.0	11.0
Zeocat (Clinoptilolite)	0.933	51.6·10 <sup>-3</sup>	66.3	12.1

and zeolite. Depending on the density of the mixture, 45–65 kg was used.

To supply oxygen to the composting materials, the reactor was connected to an air compressor, and a rotameter was used to regulate the airflow. According to the reported recommendations, airflow between 0.5 and 1 l min<sup>-1</sup> kg VS<sup>-1</sup> was supplied (Bari et al., 2000). After the thermophilic stage, the airflow was decreased. Water was added only if a significant decrease in moisture was observed. The oxygen concentration of the outlet gas was maintained at >15%. To control the temperature, heating was stopped when the temperature was greater than 65 °C.

Turnings were conducted as explained previously, and the turning frequency was decreased after the thermophilic stage. Once the cooling and maturation phase of the composting process was complete, the final product was separated from the zeolite and the composition of the compost and the zeolites were determined.

Six experiments were conducted, where the type and concentration of the zeolite was varied. Experiment E0, the control experiment, was conducted with a mixture of sewage sludge and barley straw as a bulking agent, and without zeolite. Experiments E1, E2 and E3 were conducted with a mixture of digested sewage sludge, barley straw and different types of natural zeolites (Mordenite 4/20, Klinolith and Zeocat respectively). In experiment E1, E2 and E3, the concentration of zeolite in the final mixture was 25% (wet basis). In experiments E4 and E5, clinoptilolite (Zeocat) was added in different proportions (10% and 40%, respectively).

#### 2.4. Sampling and Analysis

The duration of each experiment was set to approximately three months. The temperature inside the reactor was recorded daily, and the outlet air and the solid mixture inside the reactor were

sampled regularly throughout the experiment. The solid mixture was sampled every 6 days during the first month, every 10 days during the second month and every 15 days during the last month. Outlet gas samples were taken every day during the first week of the experiment, and the sampling frequency was gradually decreased.

To obtain 1-kg samples of solid waste, smaller amounts of waste were collected from different locations in the reactor. The sample was thoroughly mixed, and a 250-g aliquot was homogenised and used in the analysis. The remainder of the sample was discarded and returned to the reactor. All analyses were performed in triplicate.

Fresh samples were used to measure the moisture content and the pH of the sludge (in a 1:10 water extract). The remainder of the aliquot was dried and milled to achieve sludge particles with diameters less than 1 mm. The volatile solids content was obtained by determining the loss of mass after ignition at 550 °C. The carbon concentration of the dry samples was determined by dry combustion and infrared detection of CO<sub>2</sub> (Shimadzu 5050A TOC analyser). The total concentrations of nitrogen and ammonium were measured in a pre-treated dry solid sample, according to APHA standard methods (APHA, 1998). The pre-treatment for TN analyses consisted of the digestion of 0.4 g of milled, dry sample with 10 mL of H<sub>2</sub>SO<sub>4</sub> at 150 °C for 3 h in an ECO16 thermoreactor (Velp Scientifica). Pre-treatment for the ammonium analyses consisted of extraction with 2 M KCl for 30 min.

After the zeolites were separated from the final product, the compost was analysed for heavy metals. Analyses were performed on 0.5 g of milled, dry sample, which was previously treated in a microwave digester (0.5 g of dry sample and 10 mL of HNO<sub>3</sub>). The resulting liquid was diluted with deionised water and filtered, and the concentration of heavy metals was determined by ICP-mass spectrometry.

The composition of the waste (Table 1) was also determined prior to the composting experiments, and the results are shown in Table 1 as the mean value of 10 samples.

The gas inside the reactor was sampled periodically by diverting the outlet gas flow to the gas analyser, and the concentration of oxygen and NH<sub>3</sub> in the gas was determined.

After the zeolites were separated from the final compost, leaching tests were conducted to determine the ability of the zeolites to retain heavy metals. A standard leaching test for wastes derived from EPA-SW-846-method 1310 (extraction procedure toxicity test method) and reported by the Spanish official methods for hazardous waste characterisation was employed (B.O.E., 1989). Zeolites were suspended in distilled water (the weight ratio of water/zeolites was equal to 16), and the pH was adjusted to 4.5 with acetic acid. The zeolites were extracted for 24 h and vacuum-filtered with glass fiber filters. Finally, the concentration of metals in the liquid phase was analysed by ICP-Mass Spectrometry. All leaching tests were conducted in triplicate.

### 3. Results and discussion

#### 3.1. Operating conditions

Fig. 2 shows the operating conditions that were employed during the composting process. In Fig. 2a, the moisture content throughout the experiment is displayed, and the temperature of the compost over time is shown in Fig. 2b. The chart on the left in Figs. 2a and b indicates the type of zeolite used in experiments E0, E1, E2 and E3, while the graph on the right shows the effect of the zeolite concentration (experiments E0, E3, E4 and E5).

In all of the experiments, the moisture content was successfully controlled, indicating that a reactor fed with humidified air was

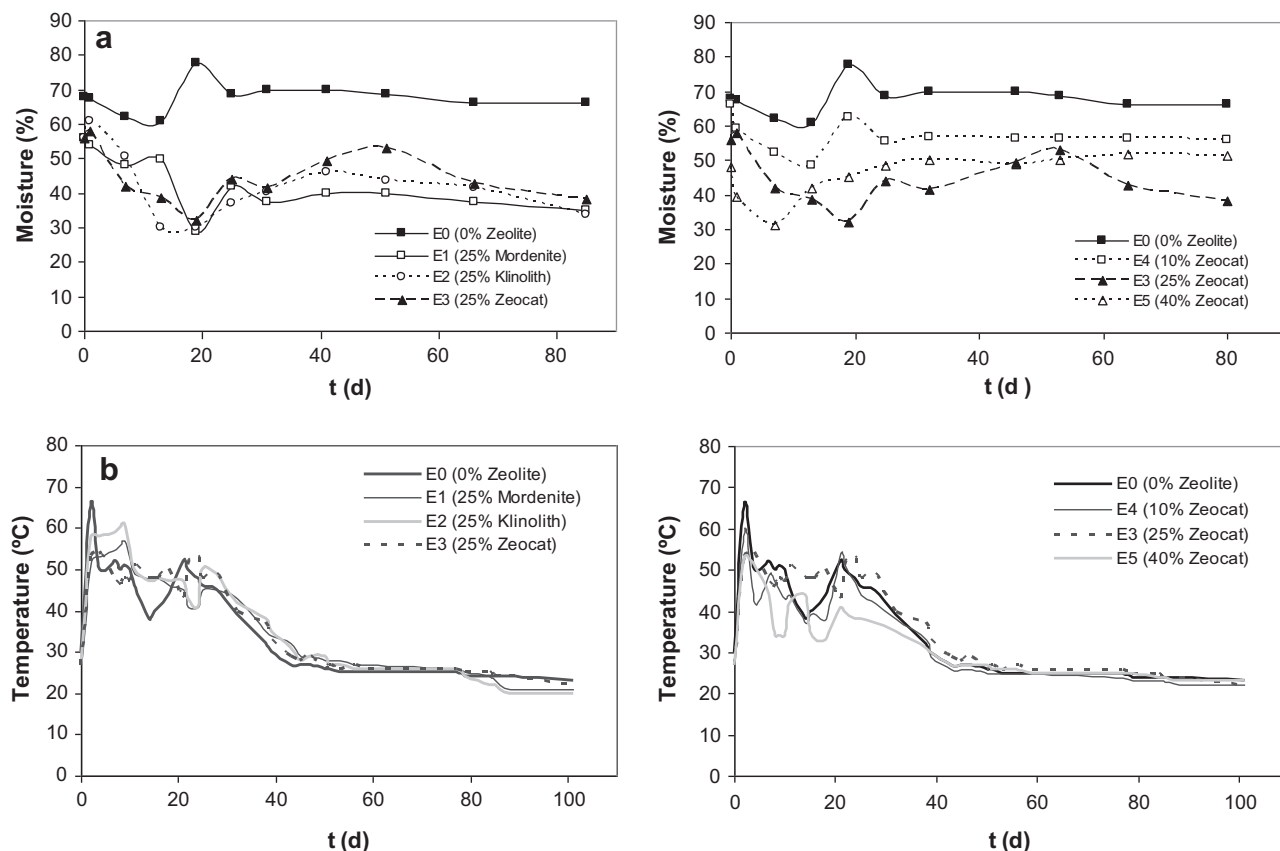


Fig. 2. The change in temperature and moisture content over time. (2a) Effect of the zeolite type; (2b) Effect of the zeolite concentration.

advantageous for composting processes (Fernández et al., 2010). Moisture was easily controlled in experiment E0, and additional water was not required. The same behaviour was observed in experiment E4, which contained 10% zeolite. As shown in Fig. 2a, the moisture content in E0 and E4 remained constant throughout the experiment.

In contrast, the moisture content clearly decreased during the thermophilic stage of experiments E1, E2, E3 and E5, and additional water was required at day 7 (E5) and day 20 (E1, E2 and E3). However, the initial moisture level of the experiments varied and was dependent on the concentration of the zeolite. After the thermophilic stage, significant changes in moisture content were not observed and additional water was not necessary.

The results indicated that water vapour was easily removed from the waste when greater amounts of zeolite were added. Similar studies (Stylianou et al., 2008; Zorpas et al., 2000a) reported that the addition of zeolites caused the sludge to retain water, and higher moisture levels were observed in the final compost. These studies also reported a bulking effect and greater porosity due to the addition of zeolites (Turan and Ergun, 2008). Despite the water retention capacity of zeolites (Knowlton and White, 1981), the bulking effect may have reduced the moisture content during the thermophilic stage of the present experiments because gases and water vapour could be removed more easily from the waste into the atmosphere. Moreover, this behaviour would only be observed at high temperatures. Alternatively, the water retention capacity of zeolites would help to maintain the desired moisture level at lower temperatures, that is, during the maturation stage. Significant differences in the results of experiments E1, E2 and E3 were not observed; thus, the type of zeolite did not affect the moisture content of the waste.

Fig. 2b shows the temperature profiles during each experiment. In all of the experiments, typical temperature changes were observed. Experiment E0 achieved a maximum temperature of 68 °C in a very short period. Moreover, high concentrations of zeolite (25% or 40%) reduced the maximum temperature of the compost. The temperature profile in E5 (40% zeolite) was quite irregular, likely due to the addition of water during periods of high biological activity. Zeolites may have reduced the potential for self-heating due to the bulking effect, which enhanced the transport of mass and energy to the atmosphere. A similar effect has not been reported in previous studies. Turan and Ergun (2008) found a bulking effect when using natural zeolites composting municipal solid waste, however a reduction in temperature was not detected. Significant differences in the temperature profiles of experiments E1, E2 and E3 were not observed, suggesting that the type of zeolite did not affect the temperature of the sludge.

The oxygen concentration of the outlet gas (results not shown) was kept above 18% during the entire composting process, such that aerobic conditions were maintained. In all of the experiments, oxygen depletion was detected during the period at maximum temperature. However, the heated airflow ensured aerobic conditions without decreasing the temperature of the waste, which was a significant advantage to the reactor design. Similar results regarding the change in the oxygen concentration of the outlet gas were obtained in a previous study (Fernández et al., 2010).

In all of the experiments, the pH decreased slightly at the beginning of the composting processes due to the formation of acids during the decomposition of organic matter (Wong et al., 1995). However, the initial pH (8.2) was nearly reached at the end of experiment E0 due to the self-regulating effect of pH, which is usually observed during composting processes. The use of higher



concentrations of zeolite appeared to acidify the compost, and a final decrease in pH was observed (the final pH was 7.1 in experiment E5); however, the effect was not significant. Turan and Ergun (2008) found also a similar pH decrease because of the addition of zeolite to a municipal solid waste composting process. Other studies did not display a clear relationship between the zeolite concentration and the pH (Stylianou et al., 2008; Zorpas et al., 2000b; Zorpas and Loizidou, 2008).

### 3.2. The concentration of volatile solids and carbon

The concentration of volatile solids (VS) and carbon (C) in the solid waste was monitored during the experiments, and VS and C losses at the end of the experiments (expressed as a percent of the initial value) were calculated and are plotted in Fig. 3. The results in the figure suggest that VS and C losses were related to the type and concentration of the zeolite. The presence of 25% zeolite (Fig. 3a) clearly increased C and VS losses; thus, the biodegradation of organic matter was improved by the addition of the zeolite. The results in Fig. 3a suggested that mordenite had the greatest effect on VS and C losses (70% and 58% respectively).

Fig. 3b revealed that higher VS and C losses were observed as the concentration of zeolite increased. This result was in accordance with the observations of Stylianou et al., (2008), who found that larger amounts of organic matter were removed when 20% zeolites were added to the waste. However, experimental variation in the present results were observed (the loss of CS and V in E5 was lower than expected); thus, this hypothesis cannot be confirmed.

To determine if the differences were statistically significant, the results shown in Fig. 3 were treated with an ANOVA analysis of variance. Four sets of one-way ANOVA analyses were performed, and the results are shown in Table 3. The analyses were performed using Microsoft Excel, and were considered significant at the 0.05 level. The results were assessed by comparing the minimum Snedecor F with the obtained F values (Miller and Miller, 1993). The results indicated that the general effects of the type and concentration of zeolite on VS and C losses at the end of the experiments were significant.

### 3.3. Nitrogen losses

Fig. 4 shows the ammonium concentration of the solid waste (dry basis) during experiments E0, E1, E2 and E3. Significant changes in the concentration of ammonium were observed during the thermophilic stage of the composting process. Microbial activity produces significant variations in the concentration of  $\text{N-NH}_4^+$  due to the transformation of organic nitrogen into ammonium and ammonia gas (Liang et al., 2006). The results revealed that the ammonium level stabilized at the end of the composting

process and compost without zeolites (E0) possessed a lower ammonium content than composts that contained zeolites (E1, E2 and E3). The results also indicated that Zeocat and Klinolith retained slightly more ammonium than mordenite in the final compost (note that the results shown in the figure correspond to the mixture, and that the zeolites had not been still separated from the final compost). According to the data shown in Table 2, Zeocat and Klinolith were more acidic than mordenite, which may be related to their ability to retain ammonium; however, the cation exchange capacities of the zeolites were similar. Based on the aforementioned results, Zeocat was selected to study the effect of the zeolite concentration.

Fig. 5 shows the losses of ammonium and ammonia at the end of the experiments, expressed as the percent of the initial concentration on a dry weight basis. The effects of the type (Fig. 5a) and concentration of the selected zeolite (Fig. 5b) are shown in the figure. Losses of ammonia gas were calculated from the ammonia concentration in the flue gas, and were verified by a mass balance from the total loss of nitrogen, according to the procedure reported by Fernández et al. (2010). Due to the design of the reactor, nitrogen could only leave the system as a gas (ammonia).

The results shown in Fig. 5a clearly illustrate the retention of ammonium by the zeolites. Both clinoptilolites halved the losses of ammonium with respect to E0. The effect of the zeolites on the emission of ammonia was not as clear as the effect on the retention of ammonium, although Zeocat appeared to be the most effective zeolite at reducing  $\text{NH}_3$  emissions. The results in Fig. 5b clearly demonstrated that the concentration of zeolite had an effect of the evolution of ammonia. As the concentration of Zeocat increased, retention of ammonium increased and emissions of ammonia gas decreased. Similarly, Witter and Lopez-Real (1988) reported that the retention of ammonium and ammonia by clinoptilolite was due to ion exchange and adsorption processes, respectively. Turan and Ergun (2007, 2008) reported that reduced ammonia losses were achieved by increasing the concentration of clinoptilolite in a composting process. They used zeolite amounts of 5% and 10%, and obtained total nitrogen losses reduction of 11% and 9% respectively.

A new ANOVA analysis, similar to the one described in section 3.2, was conducted to determine if the results were statistically significant. Four sets of one-way ANOVA analyses were performed, and the results are shown in Table 3. The results indicated that the general effects of the concentration and type of zeolite on the  $\text{NH}_4^+$  or  $\text{NH}_3$  losses at the end of the experiments were significant.

### 3.4. The Retention of Heavy Metals

Table 4 shows the concentration of metal ( $\text{mg kg}^{-1}$  dry matter) in untreated sludge and compost derived from experiment E0, E1,

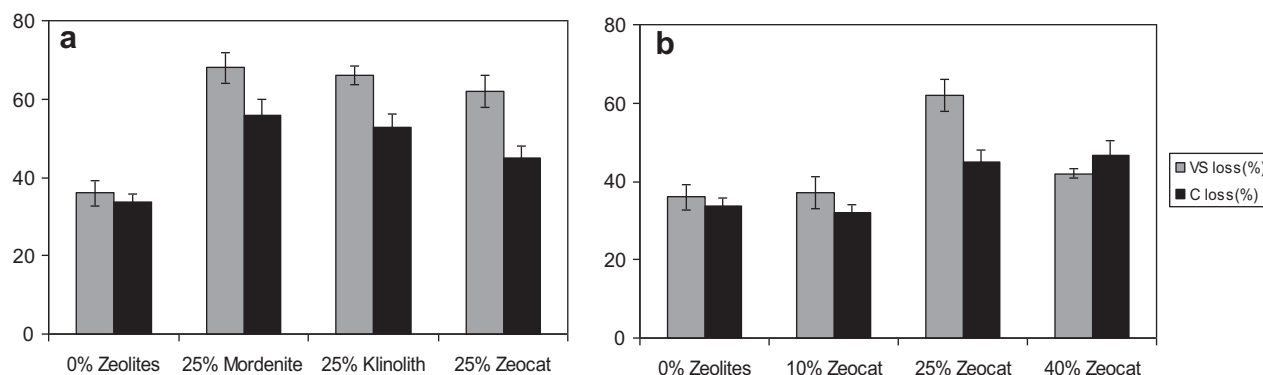


Fig. 3. Volatile solids and carbon losses at the end of the experiments. (3a) Effect of the zeolite type; (3b) Effect of the zeolite concentration.

**Table 3**Results of the one-way ANOVA analysis. The effect of the type and concentration of zeolite on the loss of VS, C,  $\text{NH}_4^+$  and  $\text{NH}_3$ .

Experiment:	Variance of data				Experiment:	Variance of data			
	VS (Fig. 3a)	C (Fig. 3a)	$\text{NH}_4^+$ (Fig. 5a)	$\text{NH}_3$ (Fig. 5a)		VS (Fig. 3b)	C (Fig. 3b)	$\text{NH}_4^+$ (Fig. 5b)	$\text{NH}_3$ (Fig. 5b)
E0	42.25	17.64	42.25	21.16	E0	42.25	17.64	42.25	21.16
E1	60.84	68.89	50.41	14.44	E4	65.61	19.36	65.61	16.81
E2	24.01	42.25	84.64	10.24	E3	70.56	38.44	49.00	37.21
E3	70.56	38.44	49	37.21	E5	6.25	54.76	30.25	11.56
Minimum $F = 3.838^*$					F obtained	12.73	7.00	9.50	62.64
F obtained	17.91	9.26	4.92	72.87	Significant differences?	yes	yes	yes	yes
Significant differences?	yes	yes	yes	yes	Least Significant difference	12.81	10.76	12.89	8.78
Least Significant difference	13.25	12.19	14.18	8.59					

\* Snedecor  $F_{4,8}$  ( $p = 0.05$ ).

E2, E3, E4 and E5 after the zeolites were removed by sieving. The results indicated that composting process E0 increased the concentration of metals in the sludge by reducing the concentration of organic matter. Moreover, metals could not leave the reactor through leaching processes.

Fig. 6 shows the efficiency of metal retention by the zeolites at the end of each experiment, which was calculated by comparing the concentration of the metal at the end of each experiment to the concentration of the metal in experiment E0. Fig. 6a shows the effect of the type of zeolite, and Fig. 6b shows the effect of the zeolite concentration.

The results indicated that the zeolites retained 100% of the Ni, Cr and Pb that was present in the sludge. Zeocat was the most effective zeolite for the removal of Cu, Zn and Hg. These results were compared to the metal retention selectivity of clinoptilolites in the literature. Zorpas et al. (2000a,b, 2003) observed the following metal retention selectivity:  $\text{Ni} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Cr}$ , while

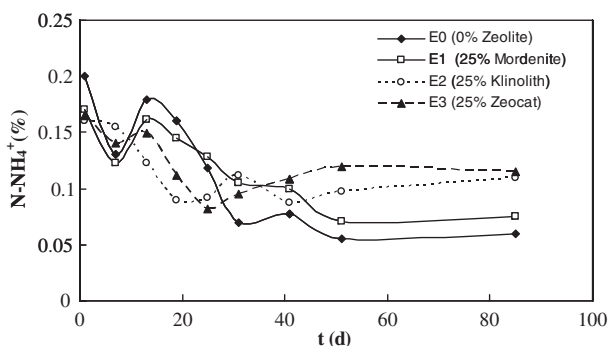
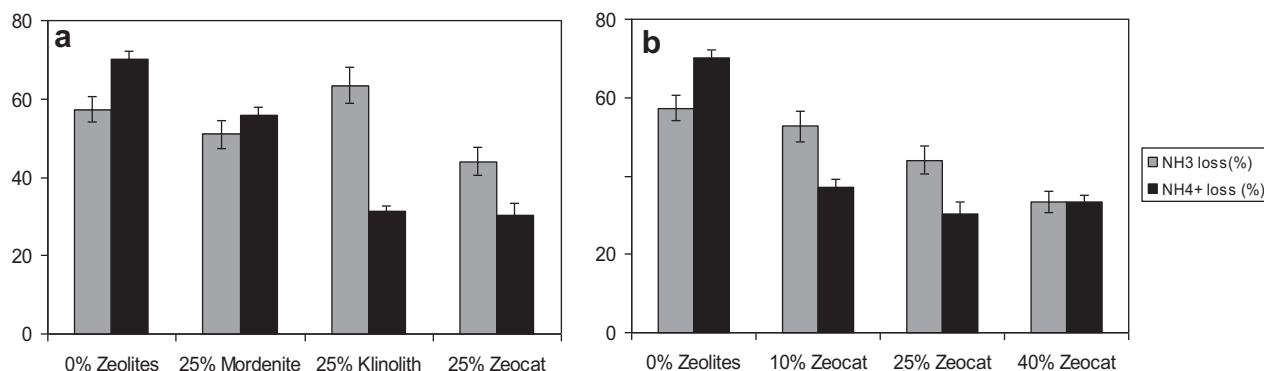
Stylianou et al. (2008) determined that clinoptilolites displayed the following selectivity:  $\text{Zn}^{+2} > \text{Cr}^{+3} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Mn}^{+2}$ . The results of previous studies and the current investigation suggested that the zeolites displayed the highest removal efficiency for Ni, followed by Pb, Cu and Zn. However, a general consensus could not be obtained for Cr retention, and Hg retention results were not available in the literature. The retention capacity of the zeolites depends on the operating conditions and the characteristics of the sludge. For instance, clinoptilolite can remove a variety of different metals from bound and exchangeable and carbonate fractions, while a significant amount of metal remains in more resistant fractions (Manios and Stentiford, 1997; Sims and Kline, 1991; Zorpas et al., 2000a). Zorpas et al. (2008) confirmed these results and reported that clinoptilolite had the ability to take up metals associated with the mobile forms such as the exchangeable and the carbonate fractions.

The results in Fig. 6b indicated that the complete retention of Ni, Cr and Pb was achieved with the addition of 10% zeolite. Moreover, the removal of Cu, Zn and Hg increased with an increase in the zeolite concentration; however, experimental variations were observed.

### 3.5. Leaching of metals from the zeolites

The results of the present study revealed that zeolites are able to retain ammonium and heavy metals; however, it was unclear whether it was preferable to remove the zeolites before applying the compost to the soil or to apply the zeolites along with the compost. Including the zeolites in the compost would increase the concentration of ammonium in the compost; however, heavy metals present in the zeolites may leach into the soil.

To determine the optimal application method, the zeolites were removed from the final compost, and leaching tests were

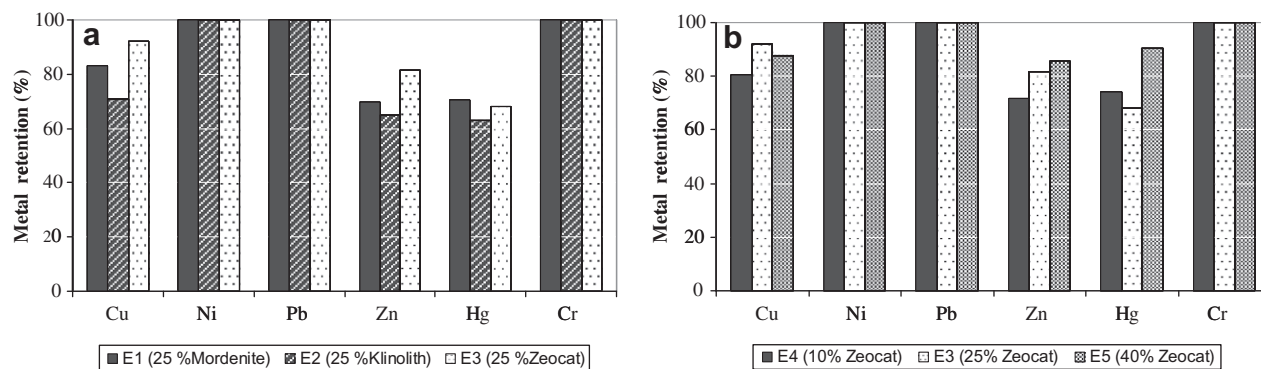
**Fig. 4.** The concentration of ammonium in the solid waste during the experiments.**Fig. 5.** Ammonium and ammonia losses at the end of the experiments. (5a) Effect of the zeolite type; (5b) Effect of the zeolite concentration.

**Table 4**

The concentrations of metal in the compost and the leachates.

Metal	Sludge conc. (mg kg <sup>-1</sup> )	Final compost concentration (mg kg <sup>-1</sup> )						Leachate concentration (mg kg <sup>-1</sup> )				
		E0	E1	E2	E3	E4	E5	E1	E2	E3	E4	E5
Cu	267.9	715.3	122.1	208.3	57.2	140.3	87.4	0.03	0.01	nd	0.05	nd
Ni	11.5	30.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pb	83.2	222.19	nd	nd	nd	nd	6.8	nd	nd	nd	nd	nd
Zn	723.4	1931.7	585.0	676.5	357.7	548.9	274.5	0.26	0.10	0.13	0.92	0.13
Hg	1.56	4.17	1.23	1.54	1.32	1.07	0.39	nd	nd	nd	nd	nd
Cr	19.0	50.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd: not detected.

**Fig. 6.** Percent metal retention at the end of the experiments.

conducted as indicated in Section 2.3. Table 4 shows the amount of metal extracted from the zeolites (as mg kg<sup>-1</sup> of zeolite), and the results suggested that low amounts of Cu and Zn leached from the zeolites. Zorpas (2009) used an acid neutralization capacity test in order to estimate the metal leachability in compost produced by using clinoptilolite as additive, and reported that by increasing the leachate pH, the heavy metal concentration decreased.

### 3.6. Compost end-use options: Direct application or zeolite separation

The last section of this paper discusses the suitability of zeolite separation before compost was applied to the soil. Compost obtained from experiment E0 contained concentrations of Hg, Zn, Pb and Cu that were higher than the maximum levels allowed by Spanish regulations (B.O.E., 2005); thus, this compost could not be applied to agricultural soils.

However, compost from experiments E1–E5 could be applied to agricultural soil if the zeolites were removed because the final zeolite-free compost was in accordance with Spanish regulations. According to the results obtained in this study, the addition of 10% Zeocat to sewage sludge produced compost that was suitable for agricultural use. Similar amounts (5% and 10%) have been recommended by other authors (Malamis et al., 2010; Turan and Ergun, 2008). Thus, to achieve compost suitable for agricultural applications: (a) metal-adsorbed zeolites should be removed from the compost or (b) metals must not be able to leach from the zeolites into the soil. The results of leaching tests shown in Table 4 indicated that leaching did not occur, except for low amounts of Cu and Zn.

To select the best application strategy, the advantages and disadvantages of each option must be considered. Zeolite separation ensures the removal of metals, and an external zeolite recovery process could be developed. On the other hand, the separation of zeolites results in the removal of significant amounts of nitrogen, decreasing the agronomic value of the compost. Moreover, the costs of zeolite separation and recovery should be considered.

The selection of the optimal compost application strategy depends on additional information that is not included in the present work, such as the behaviour of metal-polluted zeolites in soil and the cost-efficiency of zeolite removal.

## 4. Conclusions

Zeolites retained metals and ammonium in compost, and decreased ammonia emissions. Possible additional effects detected were that they improved organic matter degradation, and caused the temperature and moisture to decrease. All zeolites removed 100% of Ni, Cr and Pb, and significant amounts of Cu, Zn and Hg. Zeocat displayed the greatest retention efficiencies. The addition of 10% Zeocat produced compost that was compliant with Spanish regulations. The zeolite leachates contained very low concentrations of metals. The best strategy to the end-use of compost would depend on the leaching behaviour of the metals and the cost of the zeolite recovery process.

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