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Conference paper

AMENDMENT OF PIG SLURRY SOLIDS WITH NATURAL ZEOLITE AND ITS INFLUENCE ON STORED SUBSTRATES

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Abstract

An experiment was conducted at a 300 kg scale to observe the effect of 1% and 2% zeolite (clinoptilolite) amendment of pig slurry solids on decomposition processes during 3- month storage at ambient temperatures (8.0 - 34.7 °C). The solids were obtained by mechanical separation of slurry prior to its treatment with activated sludge.
The temperature in the piles recorded throughout the experiment exceeded 55 °C in the experimental piles and 29.8 °C in the control. The pH levels in zeolite substrates remained below that in the control for most of the thermophilic stage. A significant decrease in ammonia nitrogen ($N\text{-}NH_4^+$) in water extracts from substrates with zeolite was observed in the initial period. Changes in dry matter (DM) and ash were also recorded.

Key words: Composting, pig slurry, solid fraction, zeolite (clinoptilolite)

Introduction

Livestock slurries produced by intensive farms with a litterless system raise concern with regard to dissemination of diseases and pollution of the environment.

Liquid wastes contain high levels of nutrients, trace elements, and a variety of infective agents (Ondrašovič et al., 1990; Strauch, Ballarini, 1994). Because of their high fertiliser value they should be utilised in plant production but such practice often faces various difficulties (Ondrašovičová, 1998). If aerobic treatment is applied to animal slurries, separation of solid

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and liquid portions is usually the first process. Piggery solid wastes are nutrient rich fibrous materials readily amenable to aerobic composting (Bhamidimarri & Pandey, 1996). As they contain large proportion of organic substances inaccessible to plants and high numbers of micro-organisms and parasitic stages, biothermic treatment should precede their application to cropland (Juriš et al., 1991). However, in practice, the solid fraction (SF) is frequently stored in middens and yards where it matures under anaerobic conditions.

Zeolites are minerals with a unique structure resulting in their cation-exchange and adsorption properties. Their application in relation to animal production and environmental protection has been studied extensively from many aspects (Mumpton & Fishman, 1977, Amon et al., 1997, Bernal et al., 1993, Kithome et al., 1998).

The present study investigated the effect of two different doses of natural zeolites on stabilization processes in pig slurry solids with regard to the development of temperature in the piles and changes in selected chemical parameters from the point of view of hygiene safety of the final substrate and environmental pollution.

Materials and methods

Clinoptilolite, a natural zeolite mined at Nižný Hrabovec, Slovakia, was ground to powder (fractions: 0.38% <0.063 mm; 3.23% - 0.063-0.09 mm; 7.15% - 0.09-0.125 mm; 76.92 % - 0.125-0.250 mm; 10.77 % - 0.25-0.5 mm; 1.46% - 0.25-0.50 mm; 0.03% - 0.5-1.0 mm) and used in the study. It was pre-dried at 105 °C for 4 h.

The experiment was conducted in late spring – early summer. SF of pig slurry was obtained in the first stage of aerobic slurry treatment. After collection, the solids were transported immediately to an experimental area located at a distance of about 15 km from the farm. Four piles were set-up, two unamended controls and two zeolite-amended substrates S1 and S2 (1% and 2 % zeolite by weight, resp.). The control and zeolite-amended SF were mixed mechanically and piled up to individual compartments of a dimension of 185 cm x 93 cm. They were covered with a roof about 60 cm above the top of the substrates. The floor of the compartments consisted of concrete covered with a 15 cm layer of crushed stone on which a plastic mesh and a layer of wood chips (5 cm) was placed. Air ducts allowed free access of air to the bottom of the piles. The total weight of each pile was 300 kg and the initial height 60-65 cm. The substrates were stored for 3 months without turning or adding water to the piles. Two temperature probes (a programmable Commeter

System, Rožnov pod Radhoštěm, CR) were inserted at two symmetrical locations in each pile and the ambient temperature was recorded, too.

Samples for chemical examination were taken immediately before adding zeolite and then from the core of the substrates after 1, 2, 5, 7, 12, 21, 28, 40, 49, 61 and 84 days of storage. The samples were examined for pH (1:10 water extract) using a pH electrode, dry matter (105 °C to a constant weight), ash (550 °C /4h), water soluble ammonium nitrogen $N\text{-}NH_4^+$ by titration or photometrically after steam distillation and nitrate nitrogen $N\text{-}NO_3^-$ by an ion selective electrode and the ORION Research ionanalyser Model EA 940 in the same water extract as that used for pH determination. The analyses were performed in duplicate.

Results and discussion

Before application to agricultural land, animal manures should be stored for some time needed for decomposition of organic substances and obtaining a less odourous and hygienic material. In dependence on storage conditions organic matter is decomposed at various speeds at several temperature stages at which specific microorganisms play a dominant role. Stentiford (1996) suggested that temperatures above 55°C maximized sanitation, those between 45°C and 55°C maximized the biodegradation rates, and between 35° and 40°C maximized microbial diversity in the composting process. According to Strauch and Ballarini (1994) only the thermophilic range of 55°C is sufficient to destroy pathogens.

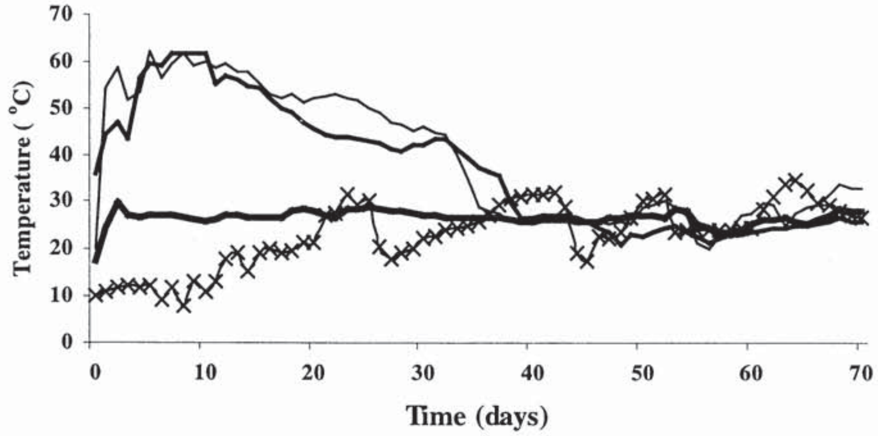
The course of temperature in individual piles is shown in Fig.1. In the zeolite-amended substrates, temperature increased rapidly and reached in 2 days 54.4°C in S1 and 44.1°C in S2 (mean ambient temperature was 10.9°C). On day 3 in S1 and on day 5 in S2 the core temperature exceeded 55°C and persisted above this level for 15 days which should be sufficient to ensure devitalization of potentially present pathogens. The highest temperatures reached in S1 and S2 were 62.1 and 61.8°C, resp. By days 35 to 38, the core temperatures in S1 and S2 substrates decreased gradually to the ambient temperature and followed its course.

The highest temperature recorded in the control was 29.8°C which is by no means sufficient to ensure hygiene safety of the final material.

Decomposition processes are affected considerably by pH. Bertoldi et al. (1983) suggested that the optimum pH values for composting are between 5.5 and 8.0. Mineralization of organic nitrogen to ammonia nitrogen may result in increase in pH while increased production of organic acids or increased nitrification may have an opposite effect.

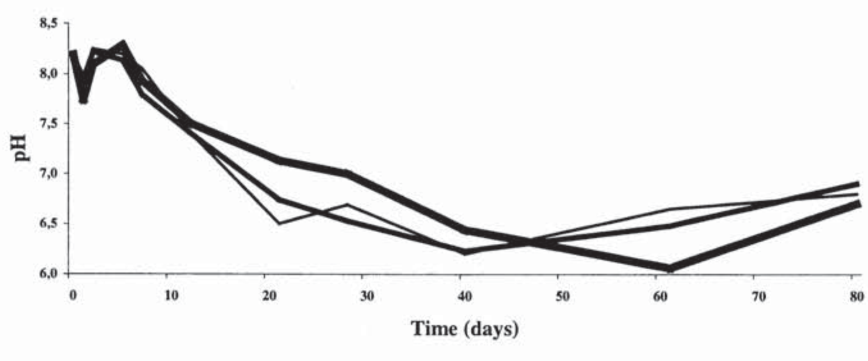
Fig. 1 - DEVELOPMENT OF TEMPERATURE IN THE CORE OF SUBSTRATES AND AMBIENT TEMPERATURE

(▬▬ = control piles, ▬▬ = pile S1, 1% zeolite by weight, ▬▬ = pile S2, 2% zeolite by weight, **x** = ambient temperature).



The pH values of all piles are shown in Fig. 2. This figure shows that the pH level in zeolite-amended substrates remained below that in the control for most of the thermophilic phase, particularly between day 20 and 40 of storage. This may be caused by affinity of zeolite to ammonium ions. Moreover, high moisture content within the piles might have created anaerobic conditions in certain layers of substrate and support production of fatty acids.

Fig. 2 - pH IN WATER EXRTRACTS OF CONTROL AND EXPERIMENTAL SUBSTRATES



(▬▬ = control piles , ▬▬ = pile S1, 1% zeolite by weight, ▬▬ = pile S2, 2% zeolite by weight).

Composting process is usually associated with loss of water as a result of evaporation. The initial moisture content will typically lie in the range of 55-65% depending on the materials being used. The maximum amount of moisture which can be tolerated varies between starting materials being limited by the inhibition of aerobic activity. On the basis of a wide range of research results it would seem that the majority of composting processes should operate with moisture contents in the 40% to 60% band (Stentiford, 1996). The initial water content in pig slurry solids subjected to our investigation was very high (77.1%). As static piles were formed, we did not expect thermophilic temperatures within the piles. However, the material itself was rather fibrous and not very densely packed and some air could be introduced during its collection, mixing and piling. The material amended with 1 and 2% zeolite was easier to handle. During the composting process DM values increased from the initial 22.9, 23.9 and 24.9% (control, S1 and S2) to the final 53.4, 59.3 and 58%, resp. (Table 1). Only after about 30 days of storage the DM content of 35% was reached in all piles above which no marked inhibition of microbial activity is expected (Stentiford, 1996). The high initial moisture content made it possible to maintain an adequate moisture up to the end of the experimental period.

Tab. 1. - DRY MATTER (%) OF SUBSTRATES

Days	0	1	2	5	7	12	21	28	40	61	84
Contr.piles	22,9	23,6	26,5	31,8	28,7	31,3	36,3	44,0	39,1	47,1	53,4
Pile S1	22,9	30,0	25,8	31,6	28,3	30,6	32,8	38,3	42,8	44,6	59,3
Pile S2	22,9	25,3	27,6	36,3	29,5	33,3	36,8	43,0	42,1	47,7	58,1

Ash (550°C) is the inorganic portion of substrates principally composed of a variety of inorganic minerals such as calcium, magnesium, sodium, iron and manganese along with other trace metals. These materials are generally unaffected by biological action and should pass through the composting process unaltered. During the biological breakdown of organic material some metabolic water and carbon dioxide are produced and a net loss in organic matter occurs. The results of ash determination are summarised in Table 1. They show a considerable difference between the control and the S1 and S2 substrates which corresponds to the intensity of decomposition processes indicated by the core temperatures.

Tab. 2. - CONTENT OF ASH (%)

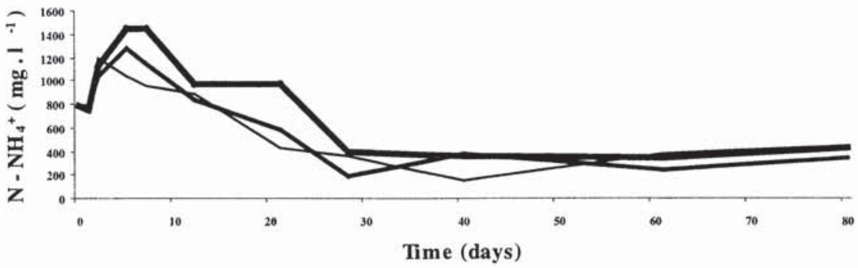
Days	0	1	2	5	7	12	21	28	40	61	84
Contr.piles	9,7	14,1	10,3	15,6	13,1	15,9	17,6	24,8	30,2	23,6	25,2
Pile S1	9,7	15,2	15,4	21,7	17,1	17,8	23,3	28,1	32,1	28,7	31,6
Pile S2	9,7	15,4	16,7	21,5	15,4	19,1	26,6	28,1	28,7	27,5	35,0

Nitrogen transformations in the first stage of decomposition of nitrogen-rich material are generally associated with high production of ammonia. The greatest nitrogen losses during composting occur in the form of NH_3. They reduce the agronomic value of the end-product but also contribute to environmental pollution.

High affinity to ammonia ions is a well-known feature of zeolites. Zeolite highly increased ammonia adsorption when added to pig slurry solids (Vargová et al. 2002). According to Bernal & Lopez-Real (1993) clinoptilolite zeolites tested by them adsorbed between 6.255 and 14.155 mg $N.g^{-1}$. Koon and Kaufmann (1975) observed impact of pH on the ammonium exchange in zeolites. For practical applications, they recommended a pH value within the interval 4-8 during the loading phase. Kitthome et al. (1998) assumed that new sorption sites were formed on zeolite at a higher pH. The initial NH_4^+ concentration and ionic-strength competition were additional factors important for ammonium exchange by zeolites (Kitthome et al., 1998). Hlavay et al (1982) observed the impact of grain size distribution on ammonium exchange capacity in the intervals of 0.5-1.0, 0.3-1.6 and 1.6-4.0 mm and reported that the smallest fraction resulted in the highest ammonium exchange capacity. According to Tiquia et al. (1997) the absence of or a decrease in $N\text{-}NH_4^+$ is an indicator of both of good composting and maturation process.

Our results of ammonium nitrogen in water extracts of investigated substrates are presented in Figure 3. During the thermophilic stage ammonia nitrogen concentration in water extracts from the control piles exceeded considerably that in the S1 and S2 piles. The greatest decrease in comparison with the control was observed on days 5, 7 and 21 in S1 and on days 7, 21 and 28 in S2. The pH levels during most of the storage were between 6 and 7.5, the range supporting maximum ion exchange. Adsorption and subsequent slow release of ammonia to the microenvironment of bacteria in the experimental S1 and S2 piles may be one of the factors that can affect the decomposition process in the piles and, at the same time, decreas the loss of nutrients from pig slurry solids stored in field heaps.

Fig. 3. - AMMONIUM NITROGEN LEVEL IN WATER EXTRACTS OF CONTROL AND EXPERIMENTAL SUBSTRATES
(▬▬ = control piles, ▬▬ = pile S1, 1% zeolite by weight, ▬▬ = pile S2, 2% zeolite by weight).



REFERENCES

1. Amon, M., Dobeic, M., Sneath, R. W., Phillips, V. R., Misselbrook, T. H., Pain, B. F. (1997): A farm-scale study on the use of clinoptilolite zeolite and de-odorase for reducing odour and ammonia emissions from broiler houses. Bioresource Technol 61, 229-237.
2. Bernal, M. P., Lopez-Real, J. M., Scott, K. M. (1993): Application of natural zeolites for the reduction of ammonia emissions during the composting of organic wastes in a laboratory composting simulator. Bioresource Technol 43, 35-39.
3. Bertoldi, M., Vallini, G., Pera, A. (1983): The biology of composting. Waste Management Res 1, 157-176.
4. Bhamidimarry, S. M. R., Pandey, S. P. (1996): Aerobic thermophilic composting of piggery solid wastes. Wat Sci Technol 33, 89-94.
5. Hlavay, J., Vigh, G., Olaszi, V., Inczedy, J. (1982): Investigations on natural Hungarian zeolite for ammonia removal. Water Res 16 (4), 417-420.
6. Juriš, P., Breza, M., Schmidtová, D., Venglovský, J. (1991): Dissemination and survival of endoparazites in the environment. Veter. Med. (Prague) 36, 665-671.
7. Koon, J. H., Kaufmann, W. J. (1975): Ammonia removal from municipal wastewaters by ion exchange. J WPCF 47 (3), 448-464.
8. Kithome, M., Paul, J. W., Lavkulich, L. M., Bomke, A. A. (1998): Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. Soil Sci Soc Am J 62 (3), 622-629.
9. Mumpton, F. A., Fishman, P. H. (1977): The application of natural zeolites in animal science and aquaculture. J Anim Sci 45, 1188-1203.
10. Ondrašovič, M., Rosocha, J., Ondrašovičová, O., Para, Ľ. (1990): Disinfection effects and changes of chemical parameters in liquid manure after addition of selected disinfectants. Bericht des 3. Hohenheim Seminars Aktuelle Probleme der Desinfection von Nutztierstallen sowie von Fest – und Flűssigmist, Stuttgart, 162-169.
11. Ondrašovičová, O. (1998): Contamination of water sources with wastes from animal production and the possibilities of their affecting (In Slovak). Habilitation Thesis, UVL Košice, 173 p.

12. Stentiford, E. T. (1996): Composting control: Principles and practice. In: De Bertoldi, M., Sequi, P., Lemmes B., Papi, T. (Eds.), The science of composting, Chapman & Hall, 49-59.

13. Strauch, D., Ballarini, G. (1994): Hygienic aspects of production and agricultural use of animal wastes. J. Vet. Med. 41, 176-228.

14. Tiquia, S. M., Tam, N. F. Y., Hodkiss, I. J. (1997): Effects of turning frequency on composting of spent pig-manure sawdust litter. Bioresource Technol 62, 37-42.

15. Vargová, M., Ondrašovičová, O., Ondrašovič, M., Sasáková, N., Falis, M., da Silva, J. A. (2002): Decomposition processes in stored pig slurry solids treated with different doses of natural zeolite. Folia Veterinaria 46 (2), Supplementum S43-S44.

DOPUNJAVANJE KRUTE FRAKCIJE TEKUĆEG GNOJA SVINJA PRIRODNIM ZEOLITIMA I NJIHOV UTJECAJ NA POHRANJENE SUBSTRATE

Sažetak

Eksperimentom se prikazuje efekt dopunjavanja krute frakcije tekućeg gnoja svinja sa 1 % i 2 % zeolitom (clinoptilolite) na procese razlaganja kroz vrijeme tromjesečne pohrane pri ambijentalnoj temperaturi (8,0 – 34,7° C). Kruti dio dobiven je mehaničkom separacijom tekućeg gnoja prije njegovog tretiranja aktivnim muljem.

Temperatura ukupne mase zabilježena za vrijeme eksperimenta prešla je 55 ° C u pokusnoj hrpi i 29,8 ° C u kontrolnoj. Razina pH u substratu zeolita ostala je ispod one u kontronoj kroz cijelo virjeme termofilne faze. Znakovito povećanje amonijevog dušika ($N\text{-}NH_4^+$) u vodenom ekstraktu iz substrata sa zeolitom promatrano je kroz neko vrijeme. Zabilježene su i promjene u suhoj tvari.

Ključne riječi: kompostiranje, tekući gnoj svinja, kruta frakcija, zeolit (clinoptilolite)

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