Application of zeolite (clinoptilolite) in the process of stabilization of the solid fraction of pig slurry.

Apport de zéolite (clinoptilolite) afin de procéder ŕ la stabilisation de la fraction solide du lisier de porc.

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Abstract

The effects of two different additions (1% and 10%) of Slovak zeolite (clinoptilolite) to the solid fraction of pig slurry was investigated under laboratory conditions. Temperature in different depth of the substrate was recorded for 42 days. Chemical and microbiological determinations of the substrates and their water extracts were carried out. The results obtained indicated some dose dependent influence of zeolite amendment on decomposition processes reflected mostly in the temperatures recorded, dry matter content and N_{total} values. The temperatures recorded in the lower third of the substrate were higher in the first stage of stabilisation for the lower addition of zeolite and in the second stage for the higher addition, in comparison with the control. The release of nutrients (N_{total}, $N\text{-}NH_4^+$) to water extract, pH and conductivity of extracts were affected, too. When compared to the control, the conductivity of water extracts determined on days 21 and 42 for the higher addition of zeolite was by 36% and 28% lower, resp., the content of ammonia nitrogen was decreased by 48% and 56%, resp., and that of total nitrogen by 43% and 47%, resp. The results obtained indicate that with regard to decomposition processes, the effects of the doses used differed, mainly in the initial stages of storage.

Key words : zeolite (clinoptilolite), pig slurry, solid fraction, microbial decomposition.

Résumé

L’effet de l’ajout de deux doses (1% et 10%) de zéolite slovaque (clinoptilolite) ŕ la fraction solide d’un lisier de porc a été étudié en conditions de laboratoire. La température ŕ différentes profondeurs a été enregistrée au cours d’une période de 42 jours. Des analyses chimiques et microbiologiques du substrat ainsi que d’extraits aqueux ont été effectués.

Les résultats obtenus suggčrent une relation et l’influence de l’ajout de zéolite sur le processus de décomposition, ŕ travers notamment l’évolution de la température, du

taux de matičre sčche et de la teneur en azote total. Les températures enregistrées dans le substrat étaient supérieures avec ajout de zéolite. Le transfert d'éléments N-total et N-ammoniacal) vers la phase aqueuse, le pH ainsi que la conductivité étaient également modifiés suite ŕ l'ajout de zéolite. Comparativement au substrat témoin, la conductivité des extraits aqueux a été mesurée aprčs 21 et 42 jours pour l'addition forte de zéolite. La conductivité était inférieure de 36% et 28% respectivement, la teneur en N ammoniacal était réduite de 48% et 56% respectivement, et celle en N total de 43% et 47% respectivement aux 2 périodes de mesure.

L'influence de la dose de zéolite apporté est particuličrement importante dans l'étape initiale de stockage du substrat.

Mots-clés : zéolite (clinoptilolite), lisier porc, fraction solide, décomposition microbienne.

1. Introduction

Large-capacity pig farms produce large quantities of slurry with high concentration of organic substances and considerable microbial contamination. The majority of pig-production facilities have been developed with little planning and concern for the nuisance and pollution characteristics inherent with their operation [1]. Most of the slurry produced by large-capacity farms in Slovakia is treated in aerobic biological wastewater treatment plants. In the first stage of the treatment, slurry is separated to the solid and liquid fractions. The liquid fraction is treated biologically and discharged to water bodies. The solid fraction, which contains considerable number of microorganisms and endoparasite eggs, should be subjected to biothermic or some other treatment before it is used in plant production [2,3]. However, the treatment of this fraction in practice consists in many cases in simple stabilization on field heaps for different periods of time. This often results in the loss of nutrients and pollution of the environment.

The aim of the present study is to investigate the influence of different additions of zeolite (clinoptilolite) on the processes of microbial decomposition and stabilization of the solid fraction of pig slurry and release of nutrients from this substrate during its storage.

2. Material and methods

The solid fraction of pig slurry, obtained by separation on vibrating screens, was mixed with powder zeolite (clinoptilolite) from Nižný Hrabovec, Slovakia (main fractions: 76.9% 0.125-0.25 mm, 10.8% 0.25-0.5 mm; CEC 0.77 mol.l^{-1}; predried at

105°C), in 1:99 and 10:90 ratio. The mixtures obtained were transferred to glass cylinders (10.5 cm i.d., 60.4 cm high) with both ends opened, placed in a vertical position in a Petri dish (containers 2 and 3, resp.) and an unamended solid fraction was used as a control (container 1). The cylinders were covered with cellulose cotton wool to prevent excessive evaporation of water

The substrates were stored at room temperature (17.0-24.0°C) for 21 days. After that time, they were removed, thoroughly mixed, and 100 g samples were withdrawn. Then they were replaced to containers and stored for additional 21 days (18.0-27.2°C). During the storage, the temperatures in the upper third, centre, and the lower third of the substrates were recorded. The liquid that oozed out of the substrates during the first 24 hours of storage was collected and analysed.

Total nitrogen (N_t), dry matter content (DM) and loss on ignition (550°C/2h) were determined in the solid fraction on day O and in all substrates after 21 and 42 days of storage. Simultaneously, determinations in water extracts were carried out (CO_2-free distilled water; 5g+45ml H_2O, diluted 1:2, for pH; 50g+250ml H_2O for determinations of N_t, $N\text{-}NH_4^+$ and conductivity).
N_t was determined by distillation and titration of $N\text{-}NH_4^+$ after previous mineralization using a HACH-Digesdahl digestion apparatus, Model 23130-20. Distillation method was also used for determination of $N\text{-}NH_4^+$ in the extracts. Conductivity was measured by means of a HACH Conductivity/TDS meter, Model 44600, and pH by means of a HACH ONE pH meter, model 43800.

Along with chemical determinations, numbers of psychrophilic, mesophilic, coliform and fecal coliform microorganisms were determined in 1 g of the solid fraction and the results were published elsewhere.

3. Results and discussion

The purpose of stabilization of farmyard manure and solid portion of slurry is to break down the organic fraction in order to reduce its mass and to obtain a product that is less odourous as well as safer from a public health standpoint [4]. Degradation of organic matter is carried out by microorganisms under aerobic, moist, and warm conditions. In dependence on the conditions of the decomposition processes (temperature, aeration, moisture, pH, content of nutrients, type of material), organic matter is degraded at different rates at several temperature phases, each of which is driven by specific groups of organisms. At optimum conditions, the temperature in the core of the substrate may reach 55-60°C, which is sufficient to inactivate pathogens and transform organic forms of N and P into inorganic forms, which are more bioavailable for uptake by agricultural crops [5].

Numerous applications of natural and synthetic zeolites have been described in different branches of industry and environmental protection. Majority of agricultural applications described concentrate on utilization of zeolites with regard to its high affinity for $N\text{-}NH_4^+$ and some metal ions and are supported by chemical determinations. In horticultural applications, the improvement in N-balance and water retention in soil is stressed after ammendment of soil with zeolites resulting in growth enhancement or yield increase of crops.

However, there are few publications in which the effects of zeolites or similar amendments are described in relation to the activity of microorganisms and acceleration or deceleration of decomposition processes [6,7].

The clinoptilolite framework consists of interconnected channels with voids big enough for water and adsorption of some ions but too small for viruses and bacteria to enter [8]. By retaining $N\text{-}NH_4^+$ ions, clinoptilolite improves efficiency in N-uptake by preventing excessive nitrification and NO_3^- leaching and helps to reduce NH_4^+ toxicity. In contrast with that, organic matter sources like peat, used as soil amendments, improve cation exchange capacity of soil but easily release ammonium ions from their exchange sites, which are then easily nitrified and thus, subjected to leaching [9].

The results obtained in our study indicate that the zeolite amendment affected the decomposition processes in the substrate investigated. During the 42 days of storage, all the substrates changed considerably and practically lost their characteristic unpleasant smell.

According to some authors [10,11], the DM content in the solid fraction obtained by separation on vibrating screens should range from 18 to about 40%. The DM content in our study was 15.75% and some retained liquid oozed out of this material during the first 24 hours of storage. The volume of the liquid released was decreased by 2.2% and 15.2% by 1% and 10% zeolite additions, respectively. Chemical analysis showed considerable differences in the parameters determined (Table 1) for original and amended solid fractions. Addition of zeolite decreased the content of N_t, $N\text{-}NH_4^+$ and electrolytic conductivity which is related to the concentration of inorganic dissolved solids, anions and cations.

	Control	1% zeolite	10% zeolite
Conductivity [$mS.cm^{-1}$]	3,83	3,55	295,00
N_{total}[$mg.l^{-1}$]	4 132,00	4 097,00	3 012,00
$N\text{-}NH_4^+$ [$mg.l^{-1}$]	3 082,00	2 976,00	2 521,00

Table 1

Analysis of the liquid released from the stored solid fraction within 24 hrs of storage

Results of chemical analysis of the solid fraction of pig slurry and amended substrates as well as of water extracts at the beginning of the experiments and after the storage for 21 and 42 days are summarised in Tables 2 and 3. Visible differences in the colour of vater extracts were observed after 42 days of storage. The extract of substrate 2 (1% zeolite) was dark-brown while that of the control (substrate 1) was yellow-brown. Grayish colouration of the extract of substrate 3 (10% zeolite) resulted from the presence of zeolite particles.

Container	1	2	3	1	2	3

	Dry matter (DM) [%]			Loss on ignition [%DM]		
Day 0	15,75			89,64		
21 days	21,42	22,38	32,78	89,02	88,75	51,78
42 days	22,10	22,34	33,89	86,90	81,10	46,93
	N_{total}[mg.kg^{-1}]					
Day 0	7018					
21 days	6445	5858	6152			
42 days	3979	4501	4487			

Table 2
Results of chemical determinations in the solid fraction of pig slurry and amended substrates

Container	1	2	3	1	2	3
	pH			Conductivity [mS.cm^{-1}]		
Day 0	7,67			4,36		
21 days	8,09	6,96	6,19	2,64	2,57	1,69
42 days	8,46	6,82	6,82	2,22	2,00	1,60
	N_{total}*[mg.l^{-1}]			$N\text{-}NH_4^+$ *[mg.l^{-1}]		
Day 0	672,3			543,5		
21 days	403,4	316,5	230,7	262,6	196,8	135,5
42 days	22,4	72,1	11,9	3,4	3,3	1,5

*Results were corrected for DM content

Table 3
Determination of chemical parameters in water extracts

The temperatures reached in the substrate exceeded the ambient temperature only by max. 2.4°C. The explanation may be found in the small quantity of the substrate and excessive moisture in its core exceeding the range 50-60%, optimal for the biothermic activity of different groups of microorganisms.

The course of temperatures differed in dependence on the depth of measurement and on the zeolite dose. In the surface layer, slightly higher temperatures were recorded in the zeolite amended substrates in comparison with the control during the most of first 21 days. The differences were more pronounced for the higher dose of zeolite (0.3-0.9°C; 0.5-1.5°C). After mixing, minimum variations around the control values were recorded.

In the centre of the substrate, for the lower dose of zeolite, the temperatures were higher by 0.3-1.0°C in comparison with the control only during the first 8 days and after that only small variations (0.1-0.2°C) were recorded always to the end. For the higher dose of zeolite, lower than control temperatures were recorded for the first 15 days (by 0.5-1.4°C), after which the temperatures increased and remained close to those recorded in the control with only small variations.

The highest differences in comparison with the control were observed in the lower third of the substrate (Figure 1). Very interesting was the course of temperatures for the lower dose of zeolite. Almost from the beginning up to day 21 (mixing), they exceeded those in the substrate with 10% zeolite and after that an opposite trend was observed.

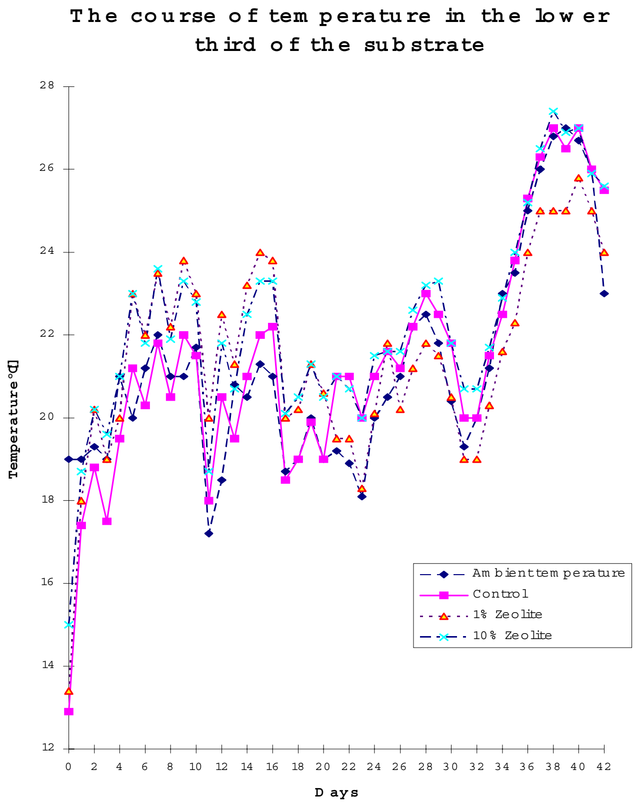

Figure 1

To confirm and explain this observation, additional investigations with larger quantity of the substrate are needed. However, the results of microbiological and chemical examination indicate that with regard to decomposition prosesses and therefore also the activity of microorganisms, the effects of the doses used differed, mainly in the initial stages of storage. The pH values measured support this assumption as well as the N_{total} values. The adsorption and ion exchange properties of zeolites were reflected in the decrease in conductivity, ammonia nitrogen and N_{total} in the water extracts and liquid that oozed out of the substrates. However, the results available provide no explanation for the change in the loss on ignition recorded after 10% addition of zeolite.

4. Conclusion

The addition of 1% and 10% zeolite (clinoptilolite) to the solid fraction of liquid slurry obtained by mechanical separation in the first stage of the slurry treatment caused changes in the release of nutrients to water extracts during the 42 days of storage and in their concentration in the fluid that oozed out of the solid fraction. A dose dependent effect on the decomposition processes was indicated.
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5. References

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