EVALUATION OF ZEOLITE AS A BINDING AGENT TO MITIGATE AMMONIA LOSS FROM PIG SLURRY AND MANURE

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1 INTRODUCTION

Nitrogen (N) in livestock food sources that does not end up in a product (e.g. milk or eggs) or that does not get incorporated in body tissue is excreted by the animal. Nitrogen in the urine is in the form of urea which can rapidly hydrolyse to form ammonium carbonate. The decomposition of ammonium carbonate frees up ammonium ions that can volatilise as gaseous ammonia (NH_3). Hydrolysis of urea is facilitated by the enzyme urease, which is abundant in soils and plant roots as well as in animal faeces. However N excreted in animal faeces is typically bound up in organic compounds which need to be mineralized to the ammonium form before NH_3 volatilisation can occur (Ndegwa et al., 2008).

The amount of NH_3 that volatises depends on factors such as the amount of N in the food source, size and species of the animal, housing conditions of the animal, humidity, temperature and animal manure handling practices. NH_3 emission from manure generated during housing and subsequent storage and spreading are nearly an order of magnitude greater than emissions from waste while the animal is grazing at pasture (Roe et al., 1998).

The work reported here considered the use of zeolite as a binding agent to mitigate NH_3 volatilisation from pig manure and slurry applied to soil. Zeolites are clay like minerals from sedimentary deposits. Zeolites selectively adsorb cations in the following order: $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} \approx Zn^{2+}$. Zeolite has been applied as a feed additive but it is more effective when applied directly to the manure (Leung et al., 2007). The hypothesis is that ammonium ions available as results of urea hydrolysis and organic N mineralization in manure will be adsorbed by the zeolite and thus reducing the volatilisation of NH_3. In addition there is an added benefit of using zeolite as a binder as it also adsorbs Cu and Zn (originating from feed) which are present in pig manure and slurry.

The aim of the proposed project was to evaluate the efficiency of using zeolite as a binding agent to reduce NH_3 volatilisation from pig slurry and manure. This was achieved by the following specific objectives:

1. To determine the effect of adding zeolite to soils mixed with pig slurry and manure on NH_3 volatilisation
2. To determine the efficacy of zeolite as an adsorbent for Cu and Zn present in pig slurry and manure
3. To determine the influence of zeolite on urease activity in soil and pig manure

2 MATERIALS AND METHODS

This project was carried out by means of laboratory experiments. The experiments were designed to pass a constant flow of water-saturated air over the top of a soil sample which had been mixed with manure and slurry. Ammonia volatilising from the soil sample was carried into a flask containing an excess of sulphate ions. Measuring the ammonium sulphate formed showed how much NH_3 had volatilised from the soil surface. The equipment used in the experiment is shown in Figure 1 and is a modification of the apparatus described by Corstanje et al. (2008). The air flow was maintained by a compressor and moved via a network of tubing to a series of equipment sets. The flow to each water flask was controlled by a needle valve. The tube entering each water flask terminated in an air stone, which served to saturate the air with water vapour. Air then passed through a flask with the soil sample and from there to the trap flask. The flasks with soil samples were operating simultaneously in a temperature-controlled environment.

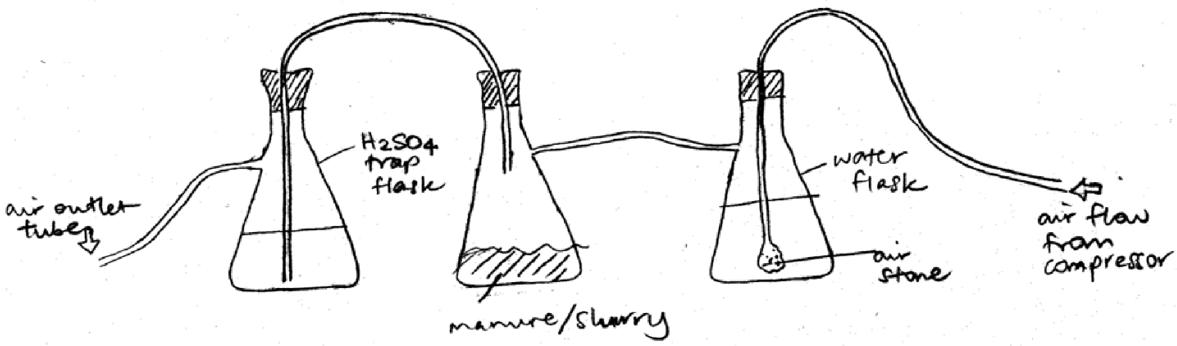


FIGURE 1 **Experimental set up for measuring ammonia volatilisation from soil**

The pig manure, slurry and soil were analysed for pH, dry matter content, N, Cu and Zn concentrations. pH, dry matter content and nutrients (carbon and N) were analysed using standard analytical equipments whilst Cu and Zn were analysed using the Atomic Absorption Spectrophotometer (AAS). The pig manure and slurry were from indoor pig units at Bedfordia in Bedfordshire, UK. The manure samples collected were mixed with straw whilst the slurry was collected from the pit within the indoor units. Soil samples were collected from the Cranfield University farm in Silsoe. The soil samples collected were free draining sandy soils to reflect the conditions where pig farms are likely to be located.

The study comprised three experiments. Experiment 1 was of NH_3 volatilisation measurements using soil mixed with manure and slurry and different rates of zeolite (5%, 10% and 15% by mass). All the treatments were replicated three times. Control experiments were also set up where the soil samples were not spiked with manure and slurry. The NH_3 volatilised was not measured directly but rather expressed as NH_4 concentrations in mM. Samples were collected from flasks as shown in Figure 1 every 24 hours.

Experiment 2 involved analysis of Cu and Zn that are usually present in manure and slurry. Zeolite can adsorb Cu and Zn and this experiment was used to determine the optimum doses of zeolite required to achieve this. Using the same set up as in Experiment 1, Cu and Zn were analysed in soil mixed with three different doses of zeolite. Soil samples were digested with aqua regia to extract Cu and Zn which were determined using AAS. Experiment 3 involved mixing soil and manure with three different doses of urea to determine urease activity in each of these combinations. Urease was determined according to the method of Corstanje et al. (2008).

3 RESULTS AND DISCUSSION

3.1 Interaction between slurry and manure with zeolite

Figure 2 shows the response of slurry and manure when amended with zeolite at 5%, 10% and 15% by mass. Figure 2 (a) shows that more NH_3 was emitted from slurry on its own than when it was mixed with soil. The difference between NH_3 emission from slurry and slurry mixed with soil was significant ($p=0.0000$) for the different doses of zeolite. Figure 2 (b) shows that the trend for manure was similar to the trend for slurry. The greater the zeolite dose the less NH_3 was emitted either from slurry or manure. However the difference in NH_3 emission from slurry, soil + slurry, manure and soil + manure was less pronounced at the greatest zeolite dose of 15%. The greatest doses of zeolite may indicate a reduction in efficiency to adsorb NH_3.

The urease activity was much greater in manure (1600-2000 μmol/g) than in soil (10-50 μmol/g) (data not shown). The urease in manure will help to hydrolyse the urea present in it to form NH_4. Figure 2 shows NH_4 concentrations in slurry and manure at the end of each experimental treatment. In Figure 2a, slurry amended with zeolite shows a significant ($p=0.0000$) reduction in NH_4 initially present. The addition of zeolite at 5% significantly reduced NH_4

after 274 h compared with 24 h. However addition of zeolite at 10% gave no difference between 24 and 274 h, although there was a large increase in-between. The addition of zeolite at 15% gave a small increase in NH_4 which was not very significant.

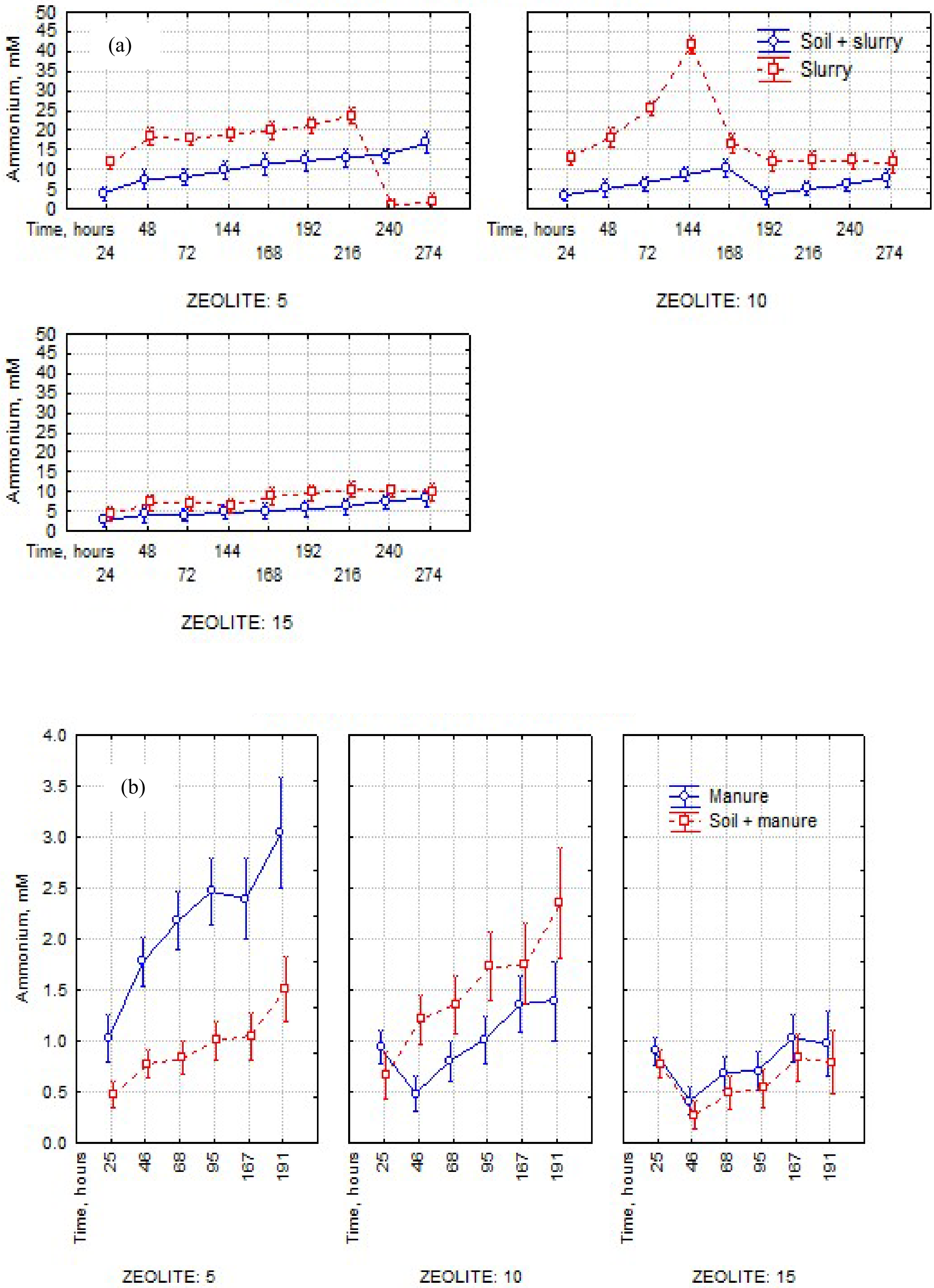


FIGURE 2 **Interaction between slurry (a) and manure (b) amended with different levels of zeolite and time on NH_4 concentrations (mM) (vertical bars denote 0.95 confidence intervals)**

This indicates that increasing the amount of zeolite may not necessarily give greater reductions in NH_3 emission. When a greater amount of zeolite was added to slurry, the adsorption of NH_4 reduced. Bernal et al (1993) found that at larger doses of zeolite, there was a reduction in its effectiveness to adsorb NH_4. A linear relationship was found between the reduction in effectiveness and the water adsorption (Bernal et al, 1993). When zeolite was mixed with slurry and soil at different levels, it did not show any significant difference. When zeolite was added to manure, similar observations were observed as with slurry (Figure 2b). High moisture content (in % mass) present in slurry (98.39±0.12) and manure (75.14±1.37) may have affected the efficiency of zeolite. Dry matter (in % mass) in slurry and manure were 1.62±0.12 and 24.86±1.37 respectively (data not shown).

Since there was no ammonium present in the soil, no control having only soil was carried out as addition of zeolite could not have had any effect on it.

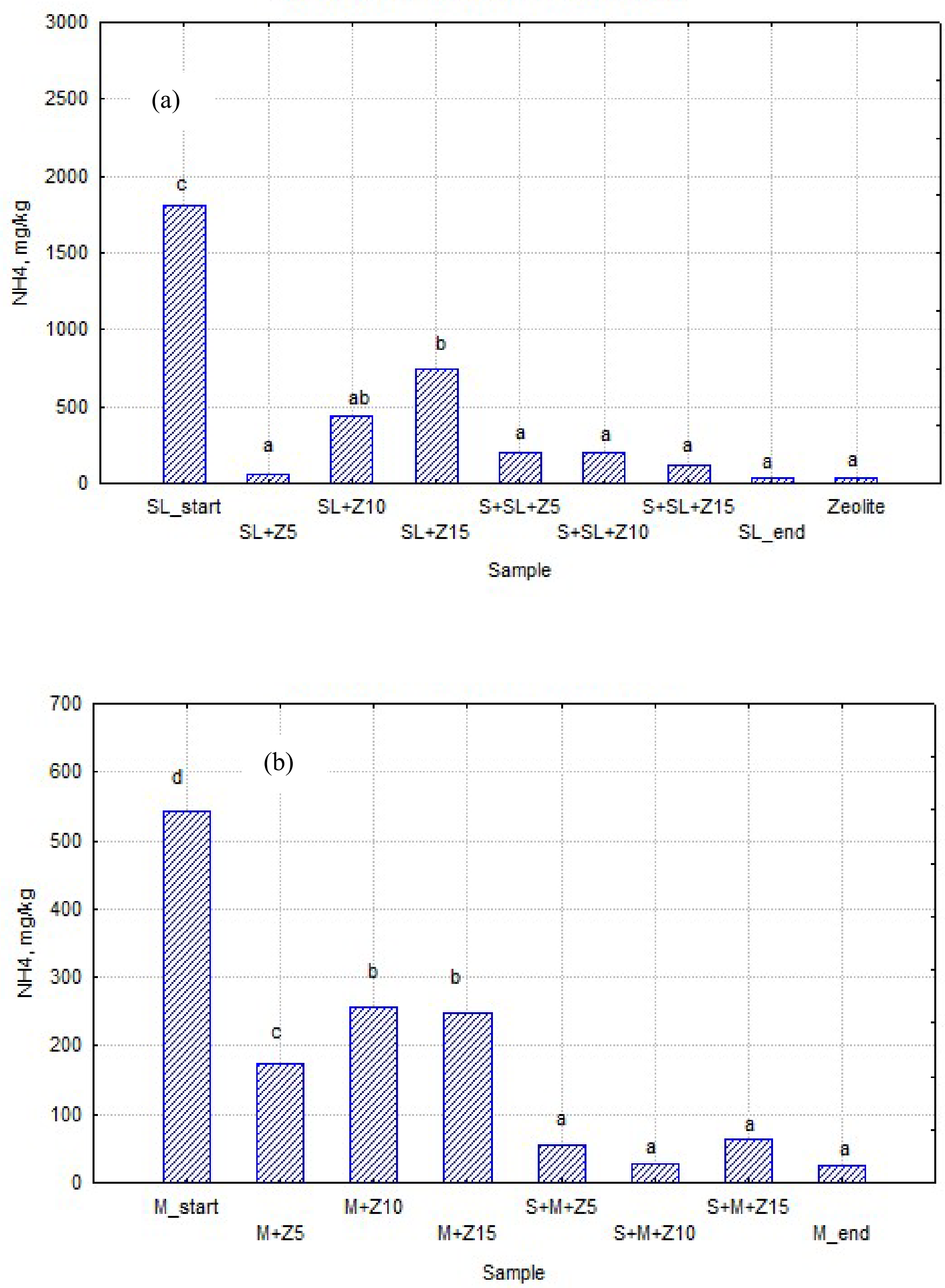


FIGURE 3 **Distribution of NH_4 in (a) slurry and (b) manure amended with zeolite (same alphabets denote statistical non significance) (SL= slurry; M= manure; Z5,Z10,Z15= Zeolite5%,10%,15%, S=Soil)**

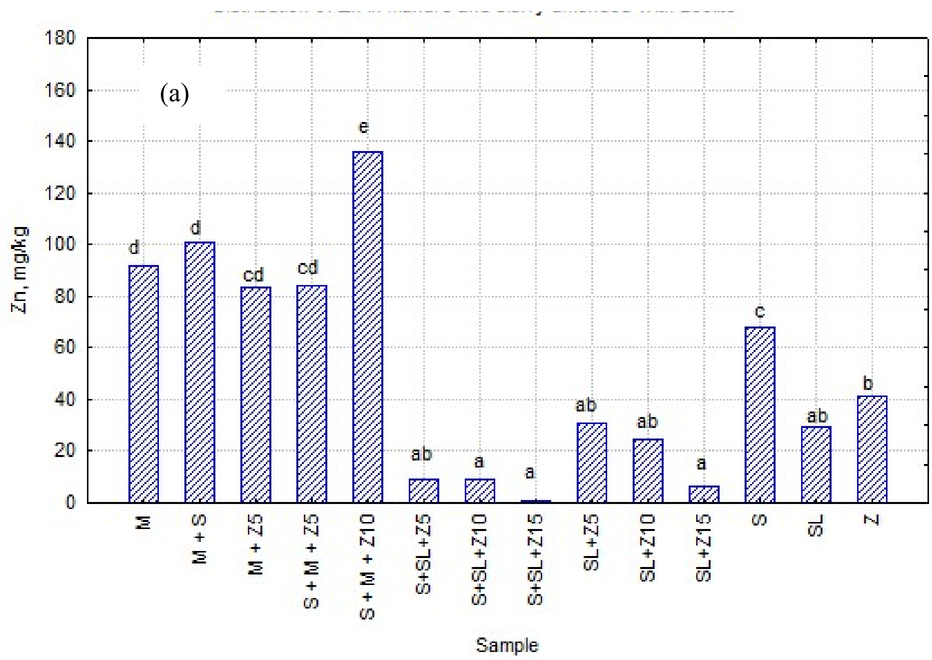
TABLE 1 **Chemical characteristics of materials used in the project (± denotes standard deviation)**

	Soil	Slurry*	Manure*
pH	5.83±0.06	7.88±0.01	7.87±0.06
Total Organic Carbon (%)	0.47±0.06	-	32.70±5.31
Total Carbon (%)	0.53±0.04	-	37.85± 3.46
Total Nitrogen (%)	0.12±0.10	-	2.23± 0.68
Dry matter content (%)	88.60±0.50	1.6±0.12	24.9±1.37
Moisture content (%)	12.90±0.55	98.4±0.12	75.1±1.37
Ammonium (mg/kg)	0	1804.56±198.24	544.21±48.71
Nitrate (mg/kg)	0.56±0.05	3.59±0.54	0.60±0.28
Cu (mg/kg)	low	low	55.28±11.25
Zn (mg/kg)	68.10±9.38	29.47±13.65	91.47±11.48

Note: ‘ – ‘ denotes not measured values; ‘low’ denotes value below detection limit using AAS;
*slurry and manure were sampled separately but all experimental setup and analysis was completed within 3 weeks

3.2 Cu and Zn dynamics in slurry and manure amended with zeolite

Figure 4 shows the Zn and Cu concentrations in manure and slurry amended with zeolite at the end of each experiment. Figure 4a shows that for Zn levels in manure, there was no significance when added with zeolite. When adding manure to soil, Zn level in Z10 was significantly higher than Z5. There was a significant difference in Zn levels in manure and slurry added with zeolite. Slurry added with zeolite did not show any significance in Zn levels. Manure added with Z5 showed a significant reduction in Cu. However Cu levels for the other treatments are not shown as its detection was too low for AAS (Figure 4b).



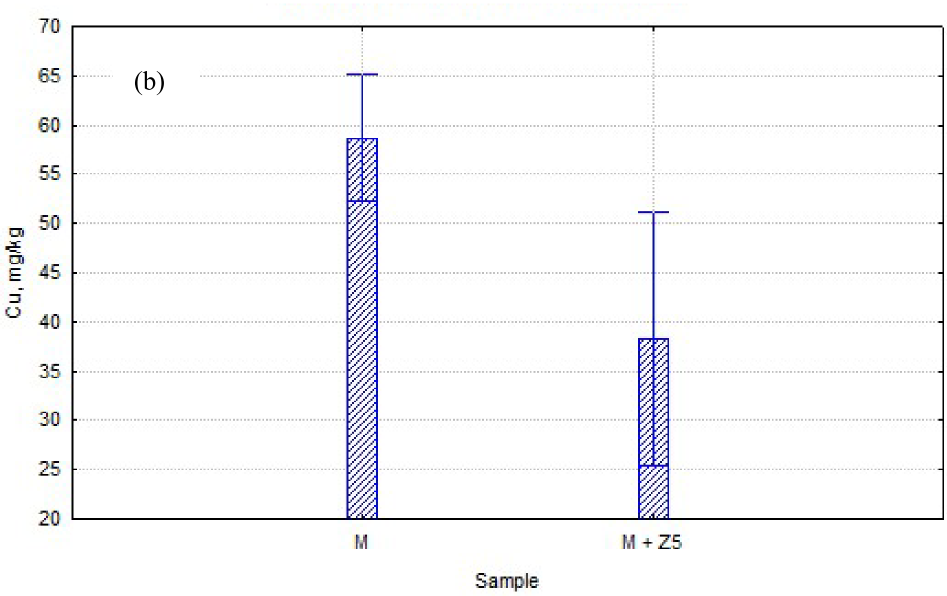


FIGURE 4 **(a) Zn and (b) Cu concentrations in slurry and manure amended with zeolite (same alphabets denote statistical non significance and vertical bars denote 0.95 confidence intervals)**

4 CONCLUSIONS

The addition of zeolite to manure and slurry reduced NH_3 emission, but greater reduction was achieved when it was mixed with soil. A higher dose of added zeolite did not increase adsorption of NH_4 as the sites of adsorption in zeolite lattice could be saturated to create any treatment effect. Zeolite was not very effective in adsorbing Zn in manure and slurry but Cu was reduced significantly (from 58 to 38 mg/kg Cu) in manure. Urease activity is greater in manure (1600-2000 µmol/g) than in soil (10-50 µmol/g) which helps to hydrolyse urea to form ammonium.

5 FURTHER RECOMMENDATION

Further experiments could be carried out to determine the rate of release of the zeolite adsorbed NH_4^+, Cu^{2+} and Zn^{2+}. This information would be vital to know the soil conditions that promote this release especially in relation to NH_4^+ which could convert to nitrate (as a slow release fertiliser) and be taken up by crops. The same principle could also be applied to Cu and Zn to meet requirements of crops as micronutrients. If the slow release capabilities of zeolite adsorbed nutrients could be explored, then this could be marketed as an alternative product to farmers. The pig farmers could exploit this as a product that they could market to the farming community.

In practical terms, the use of zeolite will be more applicable to indoor pig units where the zeolite could be added to slurry pits to reduce ammonia volatilisation. However for the outdoor pig units, zeolite could be used together with reduced* amounts of straw as bedding material in pig huts. The supply of straw is limited and hence expensive. Zeolite could be used as an alternative bedding material and has the potential to adsorbent ammonium from pig excreta and urine and later reused as a slow release fertiliser.

*Since the use of straw as bedding material is common, any use of new material has to be done in phases and hence why reduced straw is proposed rather than completely no use of straw to address any animal welfare issues.

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