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The Use of Natural Sorbents to Reduce Ammonia Emissions from Cattle Faeces

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Abstract: Intensification of animal production leads to an increase in ammonia emissions into the environment. For this reason, various methods and strategies are sought to reduce ammonia emissions from faeces. The aim of the study was to test the possibility of using natural sorbents and sorbent mixtures to reduce ammonia emissions from cattle faeces. Faecal samples for analysis were collected from Holstein-Friesian dairy cows during the winter. The amount of ammonia emissions from cow faeces was determined every seven days, after mixing the faeces with a mixture of selected sorbents. All of the sorbents used have the potential to remove ammonia. The most effective reduction in ammonia was achieved using biochar and a mixture of bentonite with zeolite. The reduction in these groups was 42.56% and 24.56%, respectively, relative to the control group. The results indicate that these sorbents can be used to reduce ammonia emissions from cattle farms.

Keywords: emission; ammonia; natural sorbents; cattle farm

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1. Introduction

Numerous gaseous pollutants, including greenhouse gases (GHG), are released during natural processes. However, expansive human activity significantly increases their presence in the environment. Carbon dioxide (CO_2), nitrogen (N) compounds, and especially nitrous oxide (N_2O) and methane (CH_4) were the first gases to be recognized as contributors to these changes [1–3]. Their most important sources, according to the Intergovernmental Panel on Climate Change (IPCC), are industry, transport, and agriculture. It is worth noting that in the next 20–50 years the global population will increase to 9.7 billion (by 25%), which necessitates major changes in agriculture and livestock production. In light of the principles of sustainable agriculture, there is a need to search for means of reducing emissions of gaseous pollutants at all stages of the food production chain [4,5]. A number of climate policy measures have recently been implemented in Europe, which is reflected in the implementation of new solutions and technologies for both land cultivation and animal farming. Production of animal protein entails emissions of gaseous pollutants. It is estimated that about 80% of ammonia (NH_3) emissions from European agriculture arise from animal excrement on farms. There are vast differences in NH_3 emissions between countries as well as between production sectors. This is due to the agricultural practices adopted for specific animal species and their yield, which influence the N cycle [6]. Emissions are lower in the case of extensive farming, due to the lower metabolic body weight of cows and greater use of pastures. Analysis of data from these farms shows a considerable decline in their number (by about 31%), while the percentage of farms with the highest herd density has increased [7]. However, the problem of noxious odours and emissions of gaseous pollutants, including NH_3, occurs on all types of farms. Available solutions have thus far involved the use of low-emission equipment or compliance with good agricultural practices. The choice of an appropriate method is determined by economic factors. Utilization of gases with chemical energy recovery on small farms entails enormous costs. Some companies propose industrial solutions for reducing emissions of volatile organic compounds (VOC) and odours, such as ColdOX^{TM} (Sävedalen, Sweden), [3,8]. According to Grant and Boehm [9], NH_3 emissions from livestock buildings mainly result from the fact that N compounds are not fully utilized for animals' growth and production. From 50% to 80% of N ingested with feed is excreted in the urine and faeces. The annual average daily NH_3 emissions are similar for different storage systems (tanks or lagoons) but are correlated with microclimatic conditions. For this reason, the authors recommend regular assessment and adjustment of production management to obtain a model that minimizes harm to the environment.

According to the EMEP/EEA guidebook (Air Pollutant Emission Inventory Guidebook), the average NH_3 emission factor (EF) from volatilization amounts to 55% of total ammonia nitrogen (TAN) in cattle slurry, irrespective of its dry matter content or pH [10]. Significantly lower EFs were obtained by Sintermann et al. [10], and therefore the authors indicate the need for changes in emissions inventories.

Emmerling et al. [11] demonstrated that acidification was the most effective method of reducing NH_3 (−69%) during storage and application of slurry and did not generate other pollutants based on N compounds. The authors also recommend combining acidification technology with other technologies, such as the use of microbial inhibitors. Slurry is acidified with sulphuric acid on farms in Denmark as a means of reducing ammonia emissions [12,13]. The authors cited tested the effects of various additives at pH 5.5 and 3.5 on the composition of pig and cattle slurry. The results showed that sulphuric acid and alum could be used in the smallest quantities to reduce the pH to 5.5 and were effective at reducing emissions of NH_3. However, as the use of strong acids entails multiple risks, we did not use acidification in our search for alternative methods.

Covali et al. [14] conducted research aimed at developing new means of reducing NH_3 emissions during storage of slurry. The authors tested various forms of biochar (BC) and acids (H_2SO_4 and H_3PO_4) that might reduce volatilization of ammonia nitrogen (NH_3-N) and increase N retention in slurry digestate. Acidified BC was shown to be an effective means of reducing NH_3-N emissions from slurry digestate. Ammonia is generated in cow sheds by the breakdown of proteins contained in excrement, uneaten feed, and bedding. Therefore, it seems worthwhile to search for solutions at this level—at the source. The substances most commonly used in practice are hydrated silicate minerals and aluminosilicates with a porous structure, such as montmorillonite and clinoptilolite, and recently BC. Montmorillonite is a clay mineral composed of packages of layers with the highest swelling capacity and adsorption capacity [15,16]. Bentonite consists mainly of montmorillonite, a clay mineral composed of three-layer structural complexes which enable absorption of ions into the inner layers. This structure gives bentonite the ability to absorb water and swell. Another aluminosilicate used is kaolin, but in this case adsorption only takes place in the surface layer. Its adsorption properties are useful in detoxifying the body and preventing diarrhoea [17], but it is crucial to take into account its place of origin, to avoid procuring material contaminated with toxins. There has recently been an increase in interest in natural and synthetic zeolites in the diet of cows. Their use during lactation protects against mycotoxins, raises pH, and reduces the level of ammonia nitrogen in the rumen [18]. The authors suggest that the level of zeolite in the diet may affect the volume of milk production and the microbiota of the rumen. The use of natural sorbents added to bedding or feed has already been tested on other animal species [19–22]. However, the choice of sorbents or components for a mixture should first be tested in laboratory conditions. Therefore, the aim of the present study was to test the possibility of using natural sorbents and sorbent mixtures to reduce NH_3 emissions from cattle faeces.

2. Materials and Methods

The study was conducted using the faeces of dairy cows collected in the winter of 2019/2020. Samples of fresh faeces were collected immediately after excretion into sterile containers and transported in thermal bags to the laboratory of the Department of Animal Hygiene and Environmental Hazards, University of Life Sciences in Lublin, Poland. Then the samples were homogenized, weighed out, and assigned to experimental groups or a control group. The experiment involved determining the amount of NH_3 released following the addition of previously selected sorbents to the faeces samples:

- Group C—control group without added sorbents;
- Group E1—with 3% addition of BC;
- Group E2—with 3% addition of bentonite;
- Group E3—with 3% addition of zeolite;
- Group E4—with 3% addition of a mixture of sorbents consisting of bentonite, zeolite and perlite in a 1:1:1 ratio;
- Group E5—with 3% addition of a mixture of bentonite and zeolite in a 1:1 ratio;
- Group E6—with 3% addition of perlite.

Faeces samples (100 g) from all groups were incubated at 24 °C in flasks modelled after Conway flasks. The concentration of released NH_3 was determined colorimetrically on the day of sample collection and after 7 (I), 14 (II), 21 (III), 28 (IV), and 35 (V) days of incubation in a Cormay Plus analyser (PZ Cormay Inc., Łomianki, Poland). The analysis was performed by an enzymatic method according to Berthelot, using Emapol diagnostic kits (Emapol Ltd., Gdańsk, Poland). The urease method is coupled with the Berthelot reaction specific for NH_3, where urease breaks urea down into CO_2 and NH_3 in the following reaction:

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3, \quad (1)$$

The absorbance, measured at 625 nm, is directly proportional to the concentration of NH_3 [23]. From each group 3 samples were collected each time and analysed in duplicate. The chemical composition of the aluminosilicates used in the experiment was determined at the laboratory of the Polish Geological Institute in Warsaw, Poland [16,19].

Statistical Analysis

Statistical analysis of the test results was carried out using Statistica v.12.0 software (StatSoft Inc., Tulsa, OK, USA). ANOVA was performed, and the significance of differences between groups was determined using the post-hoc Tukey test, for a significance level (p) of 0.05. The tables present the means (M) and standard deviation (SD).

The percentage reduction in released NH_3 was calculated for each test day (I–V) and group according to the following formula:

$$\mathrm{R}e = 100\% - [(100\% CG)/CC], \quad (2)$$

where:

R*e*—NH_3 reduction (%);
CG—amount of NH_3 released in the test group on a given test day;
CC—amount of NH_3 released in the control group on the same day [11].

3. Results

The concentrations of NH_3 released on each day of incubation, i.e., on days 0, 7 (I), 14 (II), 21 (III), 28 (IV), and 35 (V), are presented in Table 1. The concentration of total N was 0.42 ± 0.04. On the first day of analysis (day 0), the NH_3 concentration was 20.83 mg/dL. After 7 days of incubation of faeces from the control group, the NH_3 concentration was 10.54 mg/dL, which was statistically significantly higher than for Groups E1 and E2.

Table 1. Ammonia (NH_3) concentrations in the experimental groups during the study (mg/dL).

Period	C	E1	E2	E3	E4	E5	E6
I	10.54 ± 0.96 [a]	6.33 ± 0.77 [bc]	8.71 ± 0.85 [bc]	10.51 ± 1.36	11.49 ± 1.19	9.78 ± 0.68	11.09 ± 1.06
II	11.66 ± 0.97 [a]	6.75 ± 0.49 [bc]	9.58 ± 1.22 [bc]	10.33 ± 1.21	11.21 ± 0.91	9.03 ± 0.78 [bc]	10.68 ± 0.54
III	13.14 ± 1.10 [a]	6.27 ± 0.49 [bc]	8.08 ± 1.90 [bc]	10.33 ± 1.04 [bc]	11.05 ± 0.34 [bc]	8.20 ± 0.69 [bc]	11.06 ± 0.70 [bc]
IV	16.85 ± 0.60 [a]	10.57 ± 1.05 [bc]	14.93 ± 0.51 [bc]	15.78 ± 0.94	15.30 ± 1.06 [bc]	12.73 ± 1.09 [bc]	15.65 ± 1.16
V	18.24 ± 3.27 [a]	10.71 ± 0.58 [bc]	16.11 ± 0.37	16.68 ± 0.89	15.20 ± 0.30	13.06 ± 2.49 [bc]	16.21 ± 0.79

Periods: I—colorimetric determination of released NH_3 after 7 days of incubation; II—colorimetric determination of released NH_3 after 14 days of incubation; III—colorimetric determination of released NH_3 after 21 days of incubation; IV—colorimetric determination of NH_3 after 28 days of incubation; V—colorimetric determination of released NH_3 after 35 days of incubation. Groups: C—control; E1—faeces sample with 3% biochar (BC); E2—faeces sample with 3% bentonite; E3—faeces sample with 3% zeolite; E4—faeces sample with 3% mixture of sorbents consisting of bentonite, zeolite and perlite in a 1:1:1 ratio; E5—faeces sample with 3% mixture of bentonite and zeolite in a 1:1 ratio; E6—faeces sample with 3% perlite. [a–c]—Values within a row with different superscripts differ significantly ($p \leq 0.05$).

In the next measurement period (II), i.e., after 14 days, the amount of NH_3 released in Groups E1, E2, and E5 was statistically significantly lower (at $p \leq 0.05$) than in the control (11.66 mg/dL). After 21 days (III) of incubation, the highest level of the gas was obtained in the control group (13.14 mg/dL), and it was statistically significantly higher than in all experimental groups. A further increase in the NH_3 concentration was observed in the next period of incubation. It was highest in the control group, at 16.85 mg/dL, and was statistically significantly higher than for groups E1, E2, E4, and E5, at $p \leq 0.05$. The results of incubation in the final period of the experiment showed significantly higher NH_3 concentrations in the control group (18.24 mg/dL) than in groups E1 and E5 (Table 1).

Analysis of the average NH_3 levels for the entire study period revealed the highest values for the control group (14.08 mg/dL), and the lowest for Groups E1 (8.13 mg/dL) and E5 (10.56 mg/dL) (Figure 1), as the reduction in NH_3 was greatest in these groups, on average 42.56% and 24.06%, respectively (Figure 2). The lowest reduction in the level of this pollutant was obtained in Groups E3 (9.59%) and E6 (7.45%). The difference between the smallest and the greatest reduction was over 11% (Table 1).

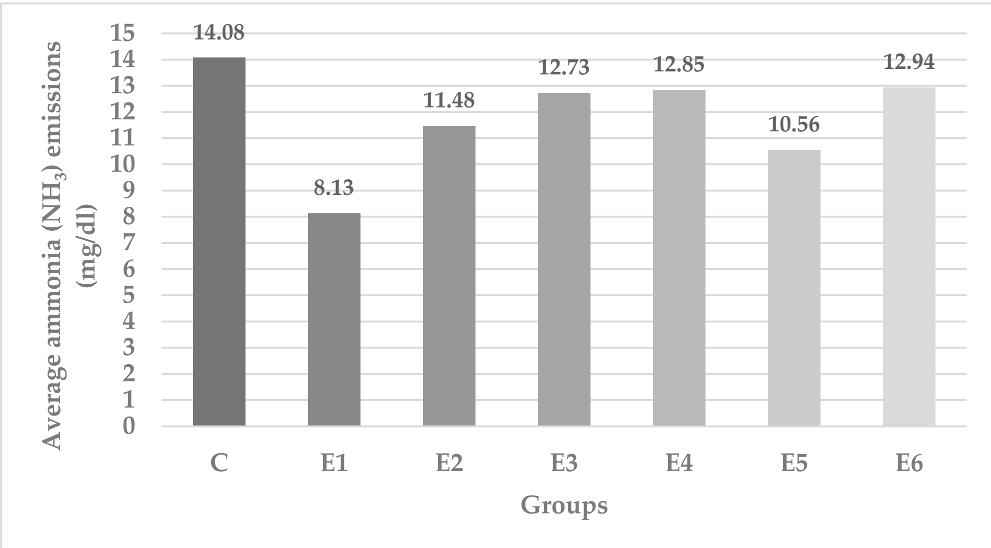

Figure 1. Average ammonia (NH_3) emissions from cattle manure during the study period (mg/dL).

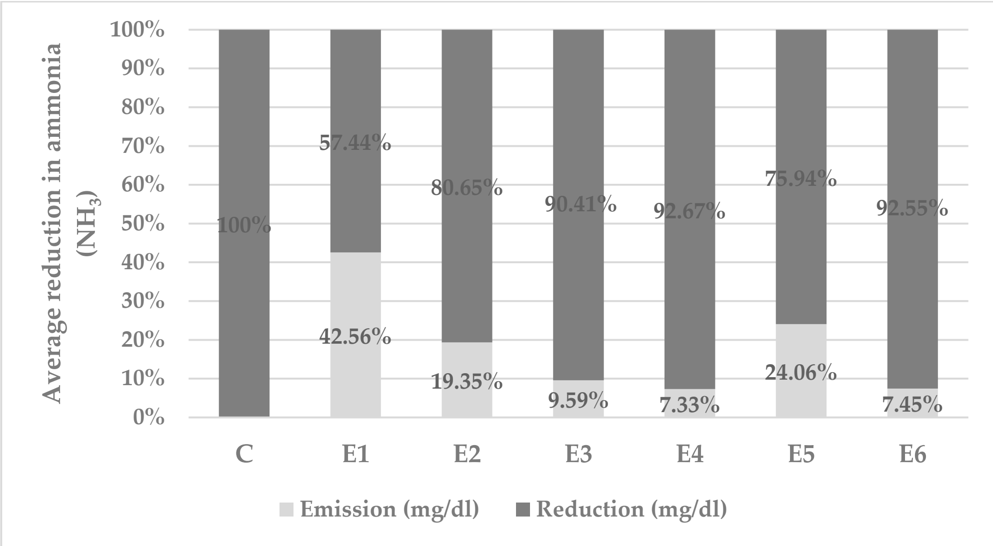

Figure 2. Average reduction in ammonia (NH_3) from cattle manure during the study period (%).

4. Discussion

Ammonia is perceived as a very important pollutant released by agriculture into the atmosphere and having a significant effect on eutrophication of natural ecosystems. Numerous EU conventions and National Emission Ceilings Directives (NECD) specify national limits on NH_3 emissions and require reports. Not all of these, however, refer to cattle farming. The EMEP/EEA contains EFs for calculating NH_3 for livestock buildings, manure storage, etc. In most cases, EFs are the weighted average of reported emissions, usually determined by scientific research. The amount of emissions varies with temperature, air movement, and humidity [24–26]. The EFs for NH_3 for dairy cows are estimated at 41.8 (slurry) and 26.4 (solid manure) kga^{-1} AAP^{-1} NH_3 [24,27]. The emissions indicator used in our study was not an annual average, as in studies by other authors, but the concentration of ammonia on the first day of analysis of the faeces samples, amounting to 20.83 mg/dL.

Backes et al. [28] compared emission reduction strategies as instruments of European policy. The authors suggest that emissions of gaseous pollutants are seasonal. A 50% reduction in emissions results in a 24% reduction in total PM 2.5 concentrations in north-western Europe. The reduction is due to reduced formation of ammonium nitrate (NH_4NO_3). Ammonia emissions decreased dramatically in the winter and increased notably in the autumn, which was due to management of manure produced during livestock farming.

The presence of gaseous pollutants in livestock buildings is a current problem, so research aimed at reducing NH_3 emissions continues. For this purpose, substances such as aluminosilicates, *Yucca schidigera* extracts, or the seaweed *Ascophyllum nodosum* are added to feed and manure to reduce the content of NH_3 in the air [29–32].

Known aluminosilicates of natural origin include zeolites, which exhibit varying selectivity towards different cations. Clinoptilolite shows significant affinity for ammonium ions (NH_4^+) and NH_3. Given to pigs together with feed, it leads to a decrease in the concentration of N compounds. Following the use of clinoptilolite, a 33% reduction in the NH_3 concentration in the air was observed, while the concentration of NH_4^+ and nitrate (NO_{3-}) ions in slurry decreased by 12–26% [29]. The decrease was slightly greater than in the present study, where the zeolite used in Group E3 caused a reduction of about 10%. Mixing zeolite with bentonite made it possible to achieve a greater reduction in NH_3—24% (E5)—but including perlite in this mixture of sorbents caused a smaller reduction. Perlite has not previously been used as a natural sorbent to reduce NH_3 emissions from cattle farms. It has, however, been added to feed to improve the bioavailability of nutrients, which helps to reduce their content in excrement introduced into the environment. It is also used in filter beds in biofilters, in order to decrease the release of gaseous pollutants on farms [33]. The sorption properties of sodium bentonite and zeolite have been confirmed for poultry manure in ex situ conditions. The greatest NH_3 reduction was obtained for 2% bentonite and 1% zeolite, and the average reduction for the entire experimental period was about 30% [20].

Shah et al. [34] added lava meal, a sandy soil top-layer, and zeolite to bedding to reduce emissions of gaseous pollutants, including NH_3. Ammonia levels at the grassland surface were measured using passive diffusion flow samplers. The average NH_3 concentration in all samples of manure treated with all additives tested was nearly 70% lower than in the control group. Further tests showed that all of the additives reduced losses of N from manure, and the increased uptake of N by plants grown in the experiment indicates improvement of the agro-environmental value of animal manure. The use of litter/manure additives has vast potential for reducing losses of gaseous N while at the same time improving crop yield. Technologies reducing emissions of pollutants through selective recovery of nutrients, especially NH_3, were tested by Ellersdorfer et al. [35], who combined stripping and ion exchange using natural zeolite. In pilot experiments with pig manure amended with various additives, Shah et al. [34] achieved 85–96% removal of NH_4^+. Montégut et al. [36] experimentally confirmed the excellent sorption properties of zeolites (clinoptilolite, chabazite and NaX faujasite) in synthetic and natural pig manure. In the present study, the presence of zeolite in the sorbent mixtures also reduced NH_3 emissions. The action of zeolite is based on a crystal structure consisting of tetrahedrons containing silicon and aluminium in various proportions, forming octahedral units. This network forms a skeletal structure with unique ion-exchange properties enabling the removal of pollutants. The efficiency of this process depends mainly on the type of pollutant, the presence of oxygen, and the reaction temperature [2].

Nuernberg et al. [22] tested the efficiency of basalt zeolite (BZ) and Cuban zeolite (CZ) in adsorption of NH_3 released from poultry manure. The zeolites adsorbed released NH_3, but CZ was more efficient than BZ, as only 5 g of CZ was needed to capture the released NH_3, compared to 20 g of BZ. This difference is explained by surface area and porosity. Biochar also exhibits very good sorption properties, and for this reason it has found applications in agriculture, environmental protection, and even medicine. It is a product obtained in the process of pyrolysis of plant biomass or biodegradable waste. It is used for plant nutrition, to improve the structure of compost, and as a carrier of microorganisms. Its properties have made it the subject of consultation and continuing research in numerous research centres. Krounbi et al. [37] used BC to transform dairy waste. The authors suggest that the manure obtained in this manner can be used in place of mineral N fertilizers, and that the BC stabilizes the solid and liquid fractions of manure, making it possible to reduce environmental pollution. Research by Covali et al. [14] using BC to reduce NH_3 indicates that acidification of slurry using strong oxidants optimizes the activity of BC. The authors indicate changes in the structure of BC under the influence of oxidants, which is of great importance when they are used as sorbents. This is due to the combined effects of carbon electrons and other functional groups of chemical substances. Marlon et al. [38] tested the properties of struvite-bearing solids from dairy wastewater, BC, and metal–organic frameworks (MOF) as sorbents for gaseous NH_3. MOF exhibited the highest sorption capacity, while the other sorbents were less effective at NH_3 sequestration. Kaikiti at al. [39] used BC produced from cattle manure to remove VOC from the manure. The results indicated the possibility of a 'cyclic economy', in which a waste product is reused. Biochar was also used by Chen et al. [40] to reduce the risk of exposure to H_2S and NH_3 during agitation of pig manure. In laboratory conditions BC in pellet form significantly reduced total emissions of H_2S and NH_3 (by ~72% and ~68%, respectively). Research aimed at reducing NH_3 emissions from cattle slurry has also been conducted by Brennan et al. [1]. The BC used in the study significantly reduced the NH_3 emissions (77%) relative to the control group. This value was also higher than in the present study. According to Brennan et al. [1], a high reduction in emissions of this gas can also be supported by controlling the pH of liquid manure. The study is a response to the need to develop a technology that can be implemented to mitigate the effect of NH_3 released from faeces on cattle farms. Guided by literature data and our own previous research in other animal species, we tested various mixtures of sorbents in order to choose the best one for future application in farm conditions. Sepperer et al. [41], who used tannin, tannin-based, and flavonoid-based absorbents to reduce NH_3 emissions from manure, found that flavonoid-based absorbents proved the most effective.

In view of the growing interest in improving air quality, the substances tested in the present study, as well as next-generation synthetic 'green' materials, can be used to reduce NH_3 emissions from cattle farms. It should be noted that the many recommendations for intensive livestock farms, issued at the national and EU level, have thus far failed to include guidelines for cattle farming. One advantage of the sorbents tested in this study is their low price. The costs of using natural sorbents to reduce ammonia emissions from faeces must be estimated separately for each country. They are linked to fees paid by farmers for polluting the environment and outlays for ongoing production. Nevertheless, the use of such additives will improve air quality on farms and in their vicinity. A potential limitation is the risk of contamination with heavy metals and dioxins, and thus it is important to consider the place of origin of the sorbents.

5. Conclusions

Emissions of gaseous pollutants generated during cattle farming and manure storage can lead not only to environmental pollution but also to a number of adverse phenomena associated with animal health and behaviour. In this study we tested the use of various sorbents and mixtures of sorbents to reduce NH_3 emissions from cattle excrement. The laboratory model experiments demonstrated a high capacity to absorb NH_3 released from faeces samples. The ex situ experiment confirmed that the 3% addition of BC (E1) and the mixture of bentonite with zeolite (E5) were the most effective at reducing NH_3 emissions. The results suggest that the sorbents tested can be used to reduce NH_3 emissions from cattle farming. However, this must be confirmed under farm conditions.

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