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Short communication

Removal of ammonia from poultry manure by aluminosilicates

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ABSTRACT

The aim of the study was to test the possibility of using aluminosilicates as natural sorbents of ammonia from poultry manure. The ammonia-absorbing properties of sodium bentonite and zeolite were confirmed in *ex situ* conditions. The most significant reduction in the level of ammonia with respect to the control was noted for 2% bentonite and 1% zeolite. The mean reduction for the entire period of the experiment ranged from 26.41% to 29.04%. The aluminosilicates tested can be used to neutralize ammonia released on poultry farms.

1. Introduction

The problem of removal of contaminated air and odours from livestock buildings, particularly on poultry farms, has yet to be solved and is a source of much controversy (Nowakowicz-Dębek et al., 2016). Maintaining optimal environmental conditions in poultry housing requires intensive air exchange, at a level of 0.5–6.0 $m^3\ h^{-1}\ kg^{-1}$. This results in substantial emissions of gas pollutants into the atmosphere. Due to the growing concentration of birds on poultry farms, the problem of removal and neutralization of waste gases from henhouses is taking on increasing importance (Sobczak and Waligóra, 2005; Hadlocon et al., 2015; Jones et al., 2013). Ammonia emissions increased dramatically in the 20th century, in some parts of the world even doubling or tripling. Research aimed at limiting the quantity of nitrogen compounds released into the atmosphere from poultry manure is conducted at numerous research centres in Europe and the United States (Jones et al., 2013; Zhang et al., 2010).

Ammonium ions (NH_4^+) in poultry litter are partitioned into an adsorbed phase and a dissolved phase. Dissolved ammonia in a liquid layer on the surface of the litter may occur in the form of ammonium ions (NH_4^+) and free ammonia (NH_3). Gas ammonia from the surface of the litter is emitted in a convection process. It exists in the atmosphere for a relatively short time, usually from a few hours to a few days, whereas ammonium ions in aerosol form can survive up to 15 days. In the atmosphere, gas ammonia usually reacts with other components to form ammonium salts, as depicted by Equations (1) and (2) (Stringfellow et al., 2009):

$$NH_3\ [g] + HNO_3\ [g] \rightarrow NH_4NO_3\ [s] \quad (1)$$

$$2NH_3\ [g] + H_2SO_4 \rightarrow (NH_4)2SO_4\ [s] \quad (2)$$

The greatest quantity of ammonia is generated on poultry farms, where annual production per bird ranges from 0.26 to 0.32 kg and 13 to 80 kg/LU (Mroczek, 2009). Excretion of nitrogen in poultry is relatively high, ranging from 1.01 to 4.80 g/day, depending on the age of the bird, and even reaching 5.4 g/day in water fowl (adult geese). In production conditions the concentration of NH_3 in the air often exceeds acceptable norms – 26 ppm, and can reach 40–60 ppm. Such concentrations are dangerous for the health of the birds, and moreover cause biological corrosion of facilities and pose a threat to the health of workers.

According to some research, ammonia emissions were detected up to 2.8 km from an intensive poultry unit (Sobczak and Waligóra, 2005; Jones et al., 2013; Mroczek, 2009). Jones et al. (2013) report that such emissions increase the total N load in the windward part of the sites by 30%, including protected areas.

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There are two main approaches for controlling and reducing pollutants: reduction at their source and removal from the flow of gases before they are dispersed in the environment (Rappert and Müller, 2005). Among the numerous methods for reducing ammonia emissions from animal production, the most noticeable effects are obtained by adding chemical preparations to the litter which neutralize emissions of ammonia and other gases, in addition to having bactericidal and deodorizing effects (Eyde, 2005; Meisinger and Jokela, 2000; McCrory and Hobbs, 2001).

As an alternative to chemical compounds, natural preparations, in the form of peat preparations, certain varieties of lignite, or aluminosilicates (bentonite, zeolites or dolomites) are increasingly used (Słobodzian-Ksenicz et al., 2008; Grela et al., 2009; Nowakowicz-Dębek et al., 2011, 2013; Wlazło et al., 2014). Aluminosilicates are a subject of increasing interest among scientists in diverse branches of industry. Clay materials have high sorption capacity, are non-toxic, inexpensive and easily accessible. Absorption by mineral compounds takes place by electrostatic ionic adsorption on the surface or adsorption within the structure of the material. The adsorption mechanism is based on electrostatic interaction, but can take place only when a molecule possesses electrically charged fragments. Research has shown that bentonite is a hydrated aluminosilicate consisting of three-layer packets. These are built of Al_2O_3 octahedrons and two outer layers of silicon SiO_2 tetrahedrons. The formula for pure montmorillonite is as follows (Eyde, 2005; Nowakowicz-Dębek et al., 2011):

$$(OH)_4 \cdot Al_4 \cdot Si_8 \cdot O_{20} \cdot nH_2O \rightarrow 2Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot nH_2O \tag{3}$$

The unique properties of this aluminosilicate result from its very high cation exchange capacity of 120–150 meq/100 g, which makes it an excellent sorbent used in water purification, the food industry, agriculture and medicine (Opaliński et al., 2009). Zeolites are characterised by a number of exceptional physicochemical properties, including high adsorption capacity, molecular sieve capacity, selectivity, ion exchange capacity, and resistance to the effects of acids and elevated temperatures. They have a well-developed surface, reaching up to 1500 $m^2\ g^{-1}$, and CEC (Cation Exchange Capacity) of 175 mg $Pb^{2+}\ g^{-1}$ and 137 mg $Cd^{2+}\ g^{-1}$. This makes them a good material for use in processes exploiting sorption and ion exchange (Bakhti et al., 2001). Besides natural zeolites, modified and synthetic zeolites are used as well. Modification of zeolites usually aims to increase their ion-exchange capacities and sorption capacity and to obtain a more selective material (Eyde, 2005; Faghihian et al., 2002). Due to their ability to absorb gases and to dry and clean air, natural zeolites are used for ventilation and to remove gas impurities from the air (Faghihian et al., 2002; Ghobarkar et al., 1999). Global utilization of natural zeolites is estimated at about 3.6 Mg $year^{-1}$. The main producers are Cuba, Germany, Japan and South Korea, and in recent years also Australia, Indonesia and New Zealand. The dominant area in which natural zeolites are used is agriculture, including animal production. A relatively new direction is the use of aluminosilicates to neutralize gas air pollutants.

The use of aluminosilicates may also be advisable on poultry farms, particularly in the winter, when the presence of ammonia is a significant problem due to inadequate ventilation of buildings (Manninen et al., 1989). The metabolic rate in gallinaceous poultry is high, and in consequence large quantities of waste and metabolites are excreted and rapidly undergo biochemical processes in the environment. Ammonia emissions in animal production are also strongly influenced by the material used as litter. Manninen et al. (1989) tested the effect of various litter preparations on ammonia concentration ex situ. Where peat was used, the ammonia concentration in the air decreased by 62% and was statistically significant. Superphosphate reduced the ammonia level by 20% and vermiculite by 28%, while in the case of pine bark it decreased by a maximum of 9%, and the results were not statistically significant. According to linear regression analysis, the ammonia concentration during the study was weakly correlated with the rate of air ventilation. Hadlocon et al. (2015) propose capturing emitted ammonia from ventilation systems of poultry buildings using a spray scrubber. The compounds can then be used to produce nitrogen fertilizer. Zápotocký and Šváb (2012), on the other hand, propose the use of a biotrickling filter. These methods, however, increase energy consumption and require appropriate installations, thereby raising production costs.

The objective of the study was to assess the use of sodium bentonite and zeolite as natural sorbents of ammonia from poultry manure.

2. Experimental procedure

Ammonia concentration was determined during incubation of faecal samples (100 g) in containers modelled after Conway diffusion cells. The samples were incubated at 25 °C. The concentration of released ammonia was determined in the laboratory on the day the samples were taken and on days 3, 6, 9, 10, 11, 12, 13 and 14 of incubation. The analysis was performed by the enzymatic method according to Berthelot using test kits by Emapol (Emapol Sp. z o.o. Gdańsk, Poland). The experiment involved determination of the amount of released ammonium when 1% and 2% by weight of sodium bentonite (referred to as experimental groups B1 and B2 respectively) and zeolite (as before, experimental groups Z1 and Z2 respectively) were added to the laying hen manure samples. The control group (K) consisted of the same material without the addition of aluminosilicates. Each sample was measured 10 times. The chemical composition of the aluminosilicates was determined in the laboratory of the Polish Geological Institute in Warsaw, and the results were presented in previous publications (Nowakowicz-Dębek et al., 2011, 2013; Wlazło et al., 2014). Statistical analysis of the test results was performed with Statistica v.6.0 software.

The reduction percentage *Re* of the ammonium released was calculated for each day according to the following formula:

$$Re = 100\% - \left(\frac{100\% \cdot CG}{CC}\right) \tag{4}$$

in which *CG* is the amount of the ammonia released in the test group on a given day and *CC* – in the control group on the same day.

3. Results and discussion

The results pertaining to reduction of ammonia from poultry manure on particular days are presented in Table 1 and in Figs. 1 and 2. In both experimental groups the aluminosilicates tested in ex situ conditions exhibited sorption properties with respect to ammonia (Table 1, Figs. 1–3). The greatest reduction in the ammonia level in comparison with the control was noted on the 9th day of incubation in groups Z1 and Z2 (Table 1), when the level of ammonia reduction was 38.74% for Z1 and 30.48% for Z2, and the results were highly statistically significant. On day 12 of the experiment considerable ammonia reduction was also obtained in group B2, at a level of 35%, and in group Z2 – 29.69%. The results were statistically significant at $p < 0.001$ (Table 1). On day 14 of the experiment the dynamics of the reaction decreased in all experimental groups, but the results were statistically significant. The mean reduction for the entire period of the experiment ranged from 26.41% to 29.04% (Table 1, Fig. 2). The smallest dispersion of values was noted in group B2 (Fig. 1). Analysis of the mean