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DETERMINATION OF AN IMPACT OF THE COMPOSITION ON THE pH LEVEL AND THE CONCENTRATION OF AMMONIUM NITROGEN IN SOIL OF PUSTOMYTY DISTRACT, LVIV REGION

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Abstract. This research involves studying the application of palygorskite from Dashukivka Deposit and clinoptilolite from Sokyrnytsia Deposit in production of organic fertilizers prolonged. It is found that maximum ammonia sorption capacity is 1.56×10^{-2} mg-eq/g of sorbents. The composition proposed has a positive impact on condition of the studied soils. The pH level of soil solution shifts toward neutral, and the level of ammonium nitrogen is uniform throughout 24 days.

Key words: ammonia, poultry manure, palygorskite, clinoptilolite, adsorption.

Introduction

Poultry farming is one of the most intensive and dynamic agricultural industries of Ukraine tending to the increase of the output of diet high-calorie products such as meat and eggs in a short term, providing people with the physiologically required nutritional norm. Poultry farming in Ukraine can be divided in two conventional sub-areas. The first one covers industrial poultry farming (large, medium and small poultry farms), incubator-poultry enterprises and rural farms. The second one includes private subsidiary farms of the population.

Specialized poultry farms operate as closed enterprises. They have capacities arranged near each facility (poultry house) designated for litter, which is removed on a daily basis by special transport means, allotted to a particular area, either to a plant for processing into sewage powder or a pit for storage with biothermal disinfection. Poultry litter is not allowed to be taken to fields without disinfection.

The negative impact of poultry farms on the environment turns up in the following ways:

 pollution of surface and ground water and soil with solid wastes and their degradation products (the total annual capacity in Ukraine is as follows: litter of natural moisture – around 5.2 mln t.; died poultry – 50 ths t.; incubation wastes – 12 ths t, poultry killing wastes – 210 ths t. [1]);

- pollution of surface and ground water and soil with wastewater concentrated with mineral and organic substances, disinfectants, insecticides, medicines, etc., generated when watering poultry, processing products, washing premises and equipment and storing and disposing wastes;
- micro- and macro-biological contamination of the environment (microorganisms, helminths, flies, etc.);
- occupation of territories for poultry farming and manure storages;
- pollution of the atmosphere with poison gases and dust, which are generated as a result of vital functioning of poultry and depend on many factors like compactness of poultry keeping, sanitary conditions in a poultry house, poultry species and age, microclimate, season, feeding, etc.

According to [2], specific and the most dangerous contamination compounds in ventilation wastes of the poultry house include ammonia, hydrogen sulphide, methylmercaptan, dimethylamine, dimethyl sulphide, caproic acid, propionaldehyde, phenol, down feather, feed dust as well as nitrogen dioxide and carbon oxide. When poultry droppings accumulate in a poultry house litter or storage, the anaerobic fermentation occurs causing the evolvement of ammonia, hydrogen sulphide and mercaptan. Based on the administrative regulations for process design of poultry houses, one square meter of litter generates around 25 mg/h of ammonia, 15 mg/h of hydrogen sulphide and 8 mg/h of carbonic acid gas. [3].

Those gases and substances affect the air quality and environmental safety. The minimum ammonia concentration adverse for human is 0.00035 mg/l. The concentration of 0.00045 mg/l causes change in brain

potential and 0.04–0.08 mg/l irritates the eyes and upper airway and entails respiratory disturbance and headache. 0.003 mg/l of ammonia inhaled by human within 8 hours cause the upset of the oxygen uptake in the body and slow down the heart rate. 0.05 mg/l of ammonia breathed in may result in fluid lungs, and the concentration of 0.35–0.7 mg/l can be fatal for human [4].

Environment pollution caused by poultry farms occurs mostly because of the inefficiency of used technologies and equipment and violation of the established ecological standards. In order to improve the environment condition in the area of poultry farming, it is necessary to take a set of actions including implementation of ecological requirements in production and systematic eco-monitoring of ventilation emissions, sewage water and animal waste generation as well as accumulation of poultry litter on the territory.

Poultry litter is a complex and non-uniform structure consisting of organic and inorganic compounds. The organic compounds mainly include nitrogenous (protein, peptides, amino acids) and carbonic (lipids, fatty acids, carbohydrates, including cellulose, sugars, alcohols, cellulose lignin) constituents. The inorganic compounds include water, ammonia, copper, phosphorous, potassium, zinc and magnesium compounds, etc. The chemical composition of litter is as follows: 22-60~% of water; 0.8-1.8~% of nitrogenous compounds; 0.4-0.9~% of P_2O_5 ; 0.7-1.3~% of K_2O .

Today there are multiple ways of poultry litter processing:

- composting;
- vermicomposting;
- litter utilization for production of biogas;
- direct litter incineration for producing heat energy;
 - high-temperature drying;
- processing by a method of extruding and granulating.

Organic fertilizers like poultry manure increase soil fertility and yielding capacity of growing products (e.g. grape, tomatoes, cucumbers, potato, cabbage, onion and garlic). However their properties degrade because of the nitrogen (N) loss, mainly due to the volatility of ammonia (NH₃). The search for ways to extend the duration of the effect and reduce the nitrogen loss during the vegetation period on account of complex fertilizers of prolonged action is carried on.

Materials and methods

The objective of our work was to determine the optimal ratio of components in a mixture of natural mineral sorbents and poultry manure and find out the effect of this composition on change of pH and the

concentration of ammonium nitrogen based on a soil type.

The experimental analyses were carried using litter from a poultry farm, consisting of hen droppings, chopped wheat straw and thin-ground CaO. The adsorbents were clinoptilolite from Sokyrnytsia Deposit and palygorskite from Dashukivka Deposit. A layout of the experimental system and the test methodology for determining ammonia in an air-gas ventilation flow are given in [5].

The efficiency of ammonia absorption from poultry manure by palygorskite and clinoptilolite was determined under the ambient air temperature of $T=20\,^{\circ}\text{C}$ and $T=15\,^{\circ}\text{C}$ with different component ratios. Results of the conducted tests are given in Table 1. It is obvious that the ammonia content degrades with the ratio "sorbent (palygorskite and clinoptilolite): poultry manure".

The next step of the test was to find the regularity of the effect of the organic-mineral fertilizing composition on change of pH and the concentration of ammonium nitrogen based on a soil type. Samples of grey, darkgrey and sod-podzolic soils were taken on the lands in Pustomyty District of Lviv Region. These types of soil are characterized by well-developed humus horizon.

Table 1

| Ratio of palygorskite + | Weight of absorbed | |
|--------------------------|--|--|
| clinoptilolite (1:1) and | ammonia, | |
| poultry manure | mg-eq $(\cdot 10^{-2})$ /g of sorbents | |
| 1:6 | 0.92 | |
| 1:5.5 | 1.2 | |
| 1:5 | 1.56 | |
| 1:4 | 1.3 | |
| 1:3.5 | 1.1 | |
| 1:3 | 0.84 | |
| 1:2.5 | 0.34 | |

Soil was sampled by an envelope method on a square plot of 10x20 meters in size at the depth of 0–25 cm, following the DSTU 4287:2004. "Soil Quality. Sampling". The selected samples were used for preparing an average sample of 1 kg. After that the soil samples were dried in a thermo-controlled dryer to an air-dry state.

Soil solution is a source of nutrients for vegetation, because plants are able to assimilate needed elements only in a diluted state.

The test method involved analyzing water extracts from soil. 50 g batches of a certain type of soil were put into 5 g dosing cups, then 5 g of composition batches were added and topped with 15 g of soil. The concentration of soil solution depends on temperature conditions and soil moisture. Therefore, the temperature

conditions were kept within 18÷20 °C, and moisture content of soil in the cups was constantly within 55 %. Water extracts were taken from samples of the mentioned soil types every three days. For that purpose we poured distilled water into an air-dry batch of soil (in the ratio of 1:5), shook it for 5 minutes and held in a stable position for 24 hours. Then the obtained solution was filtrated until the filtrate was clear. The received filtrate was the water extract from soil we used in our test. In the water extract we determined soil pH and the concentration of ammonium nitrogen.

The actual acidity is conditioned by presence of free ions in form of H^+ and OH^- in a soil solution. Determination of pH in a soil solution is essential, because the actual acidity is a factor that stipulates vital functioning of microorganisms and conditions for vegetation. Each type of soil is characterized by own reaction: for sod-podzolic soils it is acidic, for black soil it is subasidic and neutral, and for saline it is alkaline reaction.

The pH level was determined in a soil solution using a portable pH/ISE/mB/°C-meter Senslontm 2.

Our obtained results of the test of the pH level change for different types of soil are presented in Tab. 2.

Table 2
The effect of organic mineral fertilizer
composition on pH change based on soil type

| • | • | U | . . | |
|-----------------------|-------------------------------|-------------------|------------|--|
| Sampling | The pH level of soil solution | | | |
| time, within 24 hours | Sod-podzolic soil | Dark-grey soil | Grey soil | |
| 0 | 6.78 | 6.76 | 7.18 | |
| 4 | 7.35 | 7.16 | 7.18 | |
| 7 | 7.32 | 7.18 | 7.40 | |
| 11 | 7.30 | 7.20 | 7.45 | |
| 14 | 7.25 | 7.16 | 7.25 | |
| 18 | 7.32 | 7.28 | 7.46 | |
| 20 | 7.38 | 7.24 | 7.50 | |
| 24 | 7.41 | 7.29 | 7.52 | |

Potential soil fertility is evaluated by the nitrogen content. The most important inorganic types of nitrogen in soils are nitrates, nitrites, exchangeable ammonium, ammonium ions fixed in minerals, gaseous nitrogen and nitrogen oxide (I) N_2O . When the plant grows and develops, it consumes all the forms of mineral nitrogen, however the intensity of their absorption depends on soil and climate conditions. It is found that in soils with the light grain-size distribution and acidic and subacidic reaction of soil solution it is better to use the nitrite form, and in the soils with the medium and heavy grain-size distribution and neutral reaction the ammonium form of nitrogen is preferred.

Soil's mineral nitrogen is presented by exchangeable ammonium (NH⁴⁺) absorbed by soil colloids. This form of nitrogen is immovable in soil and not exposed to irrigation in the soil profile. These nitrogen forms in soil are mainly sourced from fertilization and the ammonification process (mineralization of plant remains, died off living organisms inhabiting soil, organic fertilizers). For mineral nitrogen nitrate (NO³⁻) and nitrite (NO²⁻) in the form of dissolved salts in a soil solution are used. This form of nitrogen in extremely dynamic and can be easily washed off horizontally and vertically in soil. This nitrate effect contributes to nitrogen loss from the soil layer with the active rooting zone as well as the pollution of the subsoil water.

In the air phase of soil there is gaseous ammonia (NH³+) form of nitrogen that takes part in plant nourishing too. Denitrification and ammonification processes result in formation of gaseous nitrogen forms like ammonia and nitrogen oxides diffusing in the atmosphere as well as NO₃⁻ ion washing off from the depth of the soil profile.

Ammonium nitrogen (N-NH₄⁺) was determined with the Nessler's reagent, following the DSTU 4729:2007 "Soil Quality. Determining Nitrate and Nitrite Nitrogen" using a photoelectrocolorimeter FEC -56.

The analysis results are given in Table 3.

Table 3
The effect of organic-mineral fertilizer
composition on change of the ammonium
nitrogen concentration based on a soil type

| Sampling | C (NH ₄ -N) final, mg/l | | |
|--------------|------------------------------------|-----------|-----------|
| time, within | Sod-podzolic | Dark-grey | Grey soil |
| 24 hours | soil | soil | Grey son |
| 0 | 4.09 | 6.88 | 4.09 |
| 4 | 15.11 | 4.09 | 4.09 |
| 7 | 23.72 | 16.15 | 12.01 |
| 11 | 23.72 | 16.15 | 13.91 |
| 14 | 20.28 | 23.72 | 16.15 |
| 18 | 23.72 | 20.28 | 12.36 |
| 20 | 20.28 | 23.72 | 14.77 |
| 24 | 23.72 | 27.17 | 16.15 |

Results and discussion

An analysis of the given indicators of ammonia captured from poultry manure by sorbents at different proportions, temperature and interaction duration shows that the highest capacity has been demonstrated by a composition in the proportion 1:5 at $T=20\,^{\circ}\text{C}$. It is $1.56\cdot10^{-2}\,\text{mg-eq/g}$ of sorbents.

According to the test results given in Table 2, a slight shift of the pH level in the soil solution towards the neutrality (for about 0.6 units of the pH indicator), i.e. the acidity decrease in the soil medium, has been detected in all the samples. The most favorable for

vegetation subasidic and subalkaline reaction is within pH = 6-7.5.

According to the test results given in Table 3, the ammonium nitrogen capacity, which is released during 24 hours, increased by 4 times for dark-grey and grey soil types, and 6 times for sod-podzolic soil. At the beginning of the test during the first four days the level of mineral nitrogen in the soil was law (4–15 mg/l), and after 7 days it rose to the medium level (16–24 mg/l). Within the next two weeks the level of mineral nitrogen in the soil remained medium and uniform. This shows that the offered composition is an efficient organic fertilizer of prolonged action.

Conclusion

The conducted tests prove the benefits of application of a palygorskite and clinoptilolite mixture for ammonia absorption from poultry manure with further utilization as an organic fertilizer of prolonged action. Sorbents like palygorskite and clinoptilolite added to poultry manure reduce the ammonia release into the atmosphere. Furthermore, the sorbents create favourable conditions for step-by-step nourishing of the root system with ammonium nitrogen, preventing its

possible washing off by subsoil water. This would allow decreasing the environmental hazard of atmosphere pollution with ammonium nitrogen by disposing litter from poultry farms, minimizing nitrogen loss during storage and raising the soil fertility.

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