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Research paper

Aspects of Poultry Manure Low-Emission Utilization Process

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Abstract

The article provides the results of study of an impact of poultry manure combined with a mixture of clinoptilolite and palygorskite on condition of the agricultural lands. It outlines changes in the concentration of ammonia nitrogen and phosphorus, calcium, potassium, and magnesium in soils. Also, it shows the prospects of use of the proposed composition for the purpose of utilization of poultry manure.

Keywords: *ammonia, poultry manure, palygorskite, clinoptilolite, adsorption.*

1. Introduction

Negative consequences of poultry farming for the environment in Ukraine include: air pollution with emissions of toxic gases and dust; generation of huge volumes of waste water saturated with xenobiotics; contamination of surface water bodies, soils and ground waters with accumulations of droppings and other solid waste; microbiological contamination of the environment; and retaining territories and agricultural lands for poultry farming. One of the most acute manifestations is related to the release of ammonia to the atmosphere from ventilation emissions of poultry farming premises and manure storehouses.

According to the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (1999), emissions of sulphur oxide, nitrogen oxide, ammonia, volatile organic compounds and aerosol particles affect human health, natural ecosystem, and climate as a result of transboundary transfer to large distances. In particular, Annex IX "Limit values for emissions of particulate matter from stationary sources" imposes requirements for efficient reduction of ammonium emissions at the same time with the decrease of loss of NO^{3-} and NO_2.

For recommendations on defining the best available options for reduction of ammonium emissions from farming sources please refer to [1]. Since ammonium emissions occur at each step of poultry rearing, actions on reduction of emissions must be comprehensive as well — throughout the entire nitrogen life cycle from littering to applying manure to soil. Specifically, it is outlined that ammonium emissions from droppings are minimum provided that the solid residue content is above 60% [2]. Currently, there are regulatory process operations with poultry droppings developed in Ukraine: quarantine, decontamination, and utilization [3-4].

Decontamination of droppings is performed by different methods: biothermal, thermal, chemical, physical and others.

The most common methods of utilization and recycling of poultry farming wastes are following:

- removal to fields (before using as fertilizer, poultry droppings must settle in closed containers for 2-3 years);
- composting in pits (producing high-quality biohumus);
- vermicomposting;
- thermal drying (at 65 to 1000°C) to receive powderette;
- processing by granulating;
- producing balanced organic-mineral fertilizer compositions;
- processing into feeds (dry poultry droppings are used as a feed additive for cattle);
- anaerobic and biologic fermentation using aerobic and thermophylic bacteria to produce biogas;
- direct incineration of droppings for generation of heat energy.

In general, there are two basic ways of utilization: production of organic fertilizer, and production of power. The engineering solutions above are considerably power-consuming, and require improvement and strict compliance with the process conducting conditions, and in some cases big investments. This motivates to develop new environmentally friendly technologies for processing poultry droppings.

The solution for utilization of solid wastes from a poultry farm is considered as one involving development of processes for low-emission storage and application of poultry droppings as fertilizer following international ecological agricultural regulations, implementation of which would provide additional competitive advantages to the Ukrainian agricultural industry. Application of organic fertilizers of prolonged action is of special interest as one of the ways to ensure environmentally safe and resource-saving process of crops cultivation. Studies of Dehodiuk, V. Saika, Ch. Yeanh, F. Kalinin, H. Peskovskyi, V. Shvarau, Z. Hrytsaienko, M. Yakusyk, S. Ponomarenko and others show that NPK doses meeting the requirement of environmental safety during the application of manure to soils contribute to the increase of soil productivity, improvement of agrochemical properties including the rise of microbiological activity, and enhancement of water absorbability, buffering, and other indicators defining soil bonitet.

Ukraine has two of the biggest deposits of natural mineral sorbents: clinoptilolite (Sokyrnytske, Zakarpattia Region) and palygorskite (Dashukivske, Cherkasy Region) in the world. Their advantages are availability and cheapness (e.g. 1500 UAH per 1 tone for clinoptilolite), which allow for their application in a wide range of nature-oriented processes. Both adsorbents have efficient absorbing properties because of the developed porous surface, are safe for the environment, heat resistant, possess good mechanical stability, easy to regenerate, and their industrial extraction is well established. Application of clinoptilolite and palygorskite as a mineral additive to manure does not cause additional pollution of the environment as they are natural components of the bottom sediments.

The purpose of this research was to study the prospects of use of palygorskite and clinoptilolite as adsorbents of ammonium emissions and moisture from poultry manure. The studied composition from organic fertilizer of prolonged action based on poultry manure and a mixture of palygorskite and clinoptilolite will serve as means for improvement of the soil structure. It is anticipated that this will also contribute to nitrogenous and phosphatic nutrition of the plants root system, and provide for the increased crop capacity.

In order to succeed in our objective we had to handle the following tasks:

- to study an impact of the manure composition on change in the concentration of ammonium nitrogen, phosphorus, calcium, potassium and magan, depending on a soil type;
- to determine the experimentally mechanical capacity and content of total nitrogen in a composition's granule depending on drying temperature;
- to provide a process flow diagram for utilization of poultry droppings to receive organic fertilizer of prolonged action.

2. Main body

Materials and methods. Poultry manure is a colloidal capillary-porous dark-grey substance with pungent pronounced flavour**.** This is a quick-action organic fertilizer composing of organic and mineralized ingredients. Poultry manure contains uric acid $C_5H_4N_4O_3$, ammonia, and urea $CO(NH_2)_2$. Uric acid turns into urea after a while, which decomposes naturally by urease because of vital activity of urobacteria. Urea turns into ammonium carbonate, which decomposes into ammonia NH_3 and carbon dioxide CO_2:

$$CO(NH_2)_2 + H_2O = (NH_4)_2CO_3 \quad (1)$$

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O \quad (2)$$

Such reactions occur under conditions of high temperature, pH=8÷13 and moisture content [5]. Ammonia (NH_3) formed in poultry manure is a source of environmental pollution with nitrogen. In water medium it is present as ammonium ion (NH^{4+}) and ammonia (NH_3 (wat.)), depending on pH and temperature. They are interlinked by chemical balance by the following equations:

$$NH_3(wat.) + H_2O \leftrightarrow NH^{4+} + OH^- \quad (3)$$

$$NH^{4+} \leftrightarrow NH_3(wat.) + H^+ \quad (4)$$

During storage of pure poultry manure in a dung yard, its losses can be as follows: by organic matter – up to 30-60%, by nitrogen – up to 36%, by phosphorus – 12%, by potassium – 10% [6].

Solid manure composes of organic matter by 80% (4.1% – crude fat, 14.3% – crude fibre, 46.9% – nitrogen-free extractive substances, 9.3% – aminoacids, 7.3% – admixtures), the remaining are: 4.6% – total nitrogen, 2% – total phosphorus, 1.7% – potassium oxide, 8.6% – calcium, 0.03% – copper, 0.03% – iron, 0.02% – zynk, 0.7% – magnesium, 0.3% – magnum [7]. Acidity of poultry manure is within pH=6.5÷8.0, which allows for its application to all types of soils.

Palygorskite, which is of porous structure, possesses good adsorbability as to big molecules. The mineral skeleton frame is formed of zeolite grooves 0.37×0.64 and 0.56×1.1 nm in size (primary pores) located in crystals and representing a small part of the strip. By packing, the strips form pores of different size up to 200÷300 nm long with average cross section 0.27 nm (secondary pores), i. e. are accessible for molecules of ammonia and hygroscopic water. Application of this mineral will contribute to the reduction of moisture in poultry manure and active absorption of ammonia. However, relatively low mechanical stability may restrict practical application of this clay matter as bedding.

Owing to its crystal structure, clinoptilolite is more heat-stable and acid-resistant as compared to palygorskite. It is widely known as industrial adsorbent, where ammonium ion exchange is one of the most efficient. High selectivity of clinoptilolite as to NH^{4+} can be explained by three points [8]:

- molecular size of NH^{4+} is 0.286 nm, hydrated cation size is 1.07 nm;
- cation hydration energy for compensation of surface charge is 364 kJ/g;
- average Si / Al correlation is 5.6.

Study methods. During our experiments, in order to find the ammonium nitrogen content, we used a photocolorimetry method; for the components content in a substrate we used an X-ray fluorescence analysis; also we defined static granule hardness. For our tests we prepared samples of clinoptilolite and palygorskite of the disperse content meeting the one recommended for practical application, Ø = 0.5÷1.0 mm. Fresh poultry manure was obtained from a poultry farm in form of unmodified bedding used for rearing broilers for 45 days. Sampling of grey, dark grey and sod-podzolic soils took place on the agricultural lands of the Pustomyty District in the Lviv Region (Figure 1).

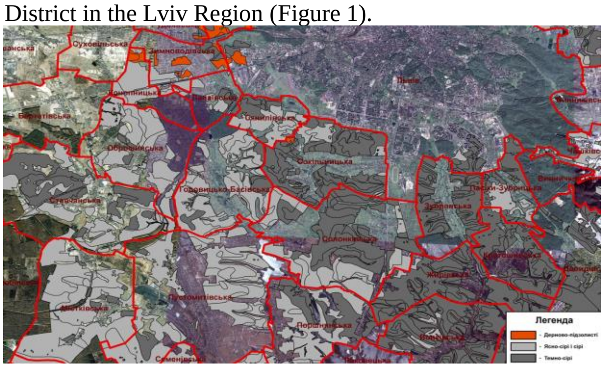

Fig. 1: Land map of the Pustomyty District in the Lviv Region.

Soil was sampled by an envelope method on a 10x20 m land plot at the depth of 0÷25 cm, following the National Standard of Ukraine DSTU 4287:2004. "*Soil quality. Sampling*".

A pattern of influence of manure composition on change in the concentration (depending on a soil type) was revealed:

- for ammonia nitrogen (N-NH_4^+) – using Nessler's reagent according to DSTU 4729:2007 *"Soil quality. Finding nitrate and ammonia nitrogen"* on photoelectric colorimeter FEK-56;
- for weight fraction of useful element (phosphorus, calcium, potassium and mangan) depending on a soil type – using energy dispersive X-ray fluorescent analyser EXPERT 3L (XRFA).

Mechanical hardness of the granule samples was determined by the methodology under GOST 21560.2.-82 *"Mineral fertilizers. Method for determination of granules static strength"* on a universal press UMM-5.

The potential soil fertility is defined by the nitrogen content in humus. The most important non-organic forms of nitrogen in soil are nitrates, nitrites, exchangeable ammonia, fixed ammonium ion in minerals, gaseous nitrogen, and nitrogen oxide (I) N_2O. Plants are nourished by the diffusive transfer of nutrient and water ions, using the root system. Ammonia and nitrate forms of nitrogen compounds are consumed.

Mineral nitrogen of soil is formed by exchangeable ammonia (NH^{4+}), absorbed by soil colloids. This nitrogen form is non-motile in soil and not exposed to washing out in the soil profile. It is sourced to soil from the application of fertilizers and ammonification (mineralisation of plant remains, died off living organisms inhabiting soil, and manure). Nitrate (NO^{3-}) and nitrite (NO^{2-}) nitrogen forms are extremely dynamic and easily washed out from the fertile soil layer by ground water in the horizontal and vertical directions.

Scientists found that nitrate form is better for use in soils with the light granulometric content, and acidic and subacidic reaction of soil solution, while ammonium nitrogen form is better for soils with the medium and heavy granulometric content, and neutral reaction. The highest nitrogen emission from soil is observed on light sandy soils, which is related to the low content of clay components. Physiological activity of ammonium fertilizers in acidic soils drops.

In earlier experiments [9] we found that a correlation of components in a mixture of natural mineral sorbents and poultry manure is optimal when adding 20% (of droppings weight) of palygorskite mixed with clinoptilolite (at 1:1 ratio). The study results are presented in Table 1.

Table 1: Influence of organic-mineral fertilizer composition on change in ammonia nitrogen concentration depending on soil type

Sampling time, day	C (NH_4-N) final, mg/l		
	Sod-podzolic soil	Dark grey soil	Grey soil
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

The study was performed using three types of soil applied with the proposed manure composition. Every three days within 24 days we analysed water extracts from the soil for the ammonia nitrogen content.

The test results given in Table 1 show that the ammonium nitrogen amount released within 24 days has increased in 4 times for dark grey and grey soil types, and 6 times for sod-podzolic soil. When at the beginning of the experiment during the first four days the level of mineral nitrogen in soil was low (4-15 mg/l), after 7 days already it rose to medium (16-24 mg/l). During the next two weeks, the level of mineral nitrogen in soil remained medium and even. This proves that the proposed composition is an efficient organic fertilizer of prolonged action.

The adsorption process includes three stages: the diffusion of sorbate molecules from flow to the external surface of sorbent grains – the external diffusion; the diffusion of sorbate molecules inside of absorbent grains – the internal diffusion; retention of absorbed molecules in the adsorption force field.

Such high results can be explained by "double" ion-exchange adsorption. Water vapour (hygroscopic moisture) in droppings easily fills grooves and cavities of clinoptilolite and the interlayer space of palygorskite. Capillary moisture together with ammonium ions can fill smaller grooves and cavities of these sorbents.

Plants assimilate phosphorus only in form of phosphate ions (PO_4^{3-}) and orthophosphate $H_2PO_4^-$. Low phosphorus content in medium results in the reduced bacteria penetration into fibrils. Lack of potassium leads to disorder in the exchange of both nitrogen and carbohydrate, and slows down phosphorus bonding with organic compounds. Under sufficient amount of calcium and magnesium in the cell medium, nitrogen-fixing bacteria remain in an active state. Lack of magnesium disturbs bacteria spreading and decreases their vital activity [10].

Concentration of the above macronutrients in the samples of background grey, dark grey, and sod-podzolic soil, and in the soil samples with the study composition after its input was changed during 24 days using energy dispersive X-ray fluorescent analyser EXPERT 3L (XRFA). The XRFA is used for excitation of atoms of a check item by external sources of ionizing radiation, followed by registration of characteristic X-ray radiation (CXRR) of atoms. CXRR energy is definitely associated with the structure of atom levels of a specific chemical element. Table 2 present the results of changes in the macronutrients concentration in the studied soil samples.

The results of the conducted experiment show that with the application of a mixture of sorbent and droppings the phosphorus content increases for both soil types (in 1.38-1.53 times). Application of the study composition stimulates the rise of the phosphorus content in 3.45 times for sod-podzolic soil, which proves its high efficiency. The potassium, calcium and mangan content for grey soil remains almost unchanged; however, for sod-podzolic soil the potassium content drops, the calcium concentration grows, and mangan remains nearly the same.

Thermal drying of droppings is performed in special plants (dryers) of various types: cylinder (concurrent and countercurrent) dryers, shaft cylinder dryers, fluidized bed dryers, contact (conductive) dryers, duct dryers, and belt dryers.

Table 2: Change in concentration of macronutrients in soil samples

Concentration of macronutrients in soil samples without nutrition			
Element	Dark grey soil	Grey soil	Sod-podzolic soil
P	1.41	0.54	0.64
K	8.59	8.77	8.58
Ca	9.94	7.0	7.31
Mn	0.67	0.50	0.42
Concentration of macronutrients in soil samples Nutrition with poultry manure			
P	1.43	0.37	1.43
K	8.41	9.0	8.2
Ca	10.73	7.0	7.31
Mn	0.56	0.50	0.47
Concentration of macronutrients in soil samples Nutrition with study composition			
P	2.165	0.75	2.21
K	8.56	9.5	8.31
Ca	9.73	7.0	7.51
Mn	0.56	0.50	0.41

Drying temperatures can vary within 80°C to 1000°C, depending on a dryer's type. High temperatures ensure compliance with such requirements. A disadvantage is the high cost of the heat-transfer medium. 1 t of droppings to be dried requires 450-500 kg of conditional fuel.

Unlike fresh poultry manure, dried manure (powderette) has low packed density (0.25-0.3 t/m^3) that is high dust-making propensity. In order to avoid this, manure must be granulated. Packed density of granulated manure is 0.6-0.65 t/m^3, which allows to reduce the storage area at least twice and enhance environmental safety for employees. Besides ammonia and ammonium ions, sorbents also absorb part of hygroscopic water from manure, providing in this way some adhesion effect. This helps to form granules effectively of a specified size

Granulation by extrusion is performed under special conditions – in a granulating press with ring and flat dies. A granulating press consists of a press mounted on a frame, and a mixer. This press is intended for producing granules by pressing with its pressing rollers through radial openings of a ring die.

Formation of granules, provided that manure is in a pseudo-liquefied condition, occurs due to dispersion of liquid manure with nozzles into a free space of a dryer, followed by pressing of the received powder. Disadvantages are:

1) inefficient decontamination from pathogenic microorganisms because of short-term keeping (15-20 s) in torch flame – microorganisms remain heat-insulated by the top layer of particles;

2) high residual moisture (within 18-20%), because pressing granulation is not possible with the lower moisture content, and non-plastic forming consistency as a consequence;
3) low packing density of the granulated product, which increases costs for packing, storage and transportation.
Heat-exchanging process during granulation in fluidized bed dryers is different from regular drying because of fluid and 10-20 µm organic particles constantly supplied to the granule surface. Heat-exchange intensity depends on air temperature and a heat medium supply rate as well as a particles size and their physical and chemical properties [13].
When drying granules under different temperature conditions, certain hardness may be provided, but cracking needs to be avoided. Granule hardness depends on preservation of the granulometric content during transportation, storage and mechanical application of the fertilizers. The study composition in form of cubes was placed in a special mould with 15×15×15 mm cells. The obtained samples were kept for 24 hours to achieve a fixed form. The formed cubes were dried in two ways: in a drying oven (T = 80°C; 105°C; 140; 200°C) until constant weight during 6 hours, and under a vent hood during one day at T=20°C. The results of determination of static hardness and the relative moisture content of the granules are presented in Table 3.

Table 3: Granule static hardness data in accordance with *GOST 21560.2.-82*, kg f/m^2

Granule No.	T = 20°C	T = 80°C	T = 105°C	T = 140°C	T = 200°C
1	55	62	60	80	66
2	65	72	75	78	78
3	48	68	86	82.5	63
4	45	64	84	81	80.6
5	52	69	76	80	71
6	64	70	84	79	73
Average	54.83	67.5	77.5	80.08	71.9
Relative moisture, %	57.0	44.92	37.67	30	28.27

The study results show that with the increase of drying temperature to T = 140°C mechanical hardness of the granules rises in 1.46 times.
In process of drying of poultry manure granules at T=105°C, we observed pungent, strong foul smell enhancing throughout the test. Immediately after adding the sorbents the smell disappears, and does not occur throughout the process of drying the granules with the sorbents at different temperatures (80-140°C). This can be explained by following: moisture from poultry manure is actively absorbed by the sorbents; therefore, microorganisms cannot spread and release new portions of ammonia. At the same time, absorbed ammonia is also adsorbed strongly enough at the active centres of minerals, and its desorption does not occur in the specified temperature range. Our moisture weight fraction determination method was based on defining the weight loss of a manure sample stipulated by drying to constant weight in a drying oven (following GOST 26713-85 "*Organic fertilizers. Method for determination of moisture dry residue*") under different temperature conditions. We observed significant reduction of the moisture content of 15×15×15 composition granules – moisture weight fraction in the final product was 28 to 45%.
Poultry manure refers to waste of Hazard Class III and is included in Waste Group 01, its classification grouping is 012, code: 0124.2.6.03 "Poultry manure" [11]. We believe an efficient method for utilization of poultry droppings is granulation followed by drying. Advantages of this process are following:
- time saving because of excluding a stage where fresh poultry manure is kept in pits (for several months); the fertilizer is almost sterile and free from pathogenic organisms and weeds;
- dried manure at relatively low temperatures contains 80-85% of organic matter, 4-5.5% of nitrogen, 2.6-2.8% of P_2O_5, and 1.3-1.8% of K_2O;
- after thermal drying, manure weight drops in 3-4 times, resulting in substantial cut of storage and transportation costs;
- today, all agricultural machines are fully equipped for application of fertilizers in a granulated form.

A process flow diagram for production of organic fertilizer of prolonged action would consist of the following stages:
1) removal of solid mechanical impurities by grinding manure to 6-8 cm;
2) mixing in a mixing grinder;
3) granulating an obtained mixture in a closed screw granulator to granules 4-6 mm in diameter and 15-20 mm long;
4) drying granules until the moisture content is 12-15% in a drying cylinder by countercurrent flow at T = 145-80^{0}C;
5) packing in a commercial fraction.

Poultry manure is delivered to a feed hopper by a tractor trailer and loaded to a receiver. During accumulation in a dung yard, manure can get separated into liquid and solid fractions by itself, unevenly changing the moisture content of raw product before granulation by extruding. Feather, shell, small rock and lime remains over 1 mm in size impede the process of granule formation and drying. This can cause induced and lasting delays in the process because of a necessity to clean the consistence from those solid impurities. This operation can be performed for example by a special device [12].
A mixing grinder is used for grinding and mixing viscous paste materials with dry additives. In this process flow diagram we propose adding components to poultry manure at a ratio "50:10 = manure: sorbents (clinoptilolite : palygorskite = 5:5)". From hoppers for natural dispersive sorbents clinoptilolite and palygorskite are supplied in grains of 0.5-1 mm in diameter and dosed by feeders to a mixer.
An obtained mixture from the mixer is forwarded by a feeding mechanism to a closed screw granulator. Each of the sorbents actively absorbs moisture and ammonia from this solid waste. Poultry manure is naturally adhesive and therefore does not require additional agents to enhance adhesion with the sorbent surface. The proposed composition is pressed by pressing rollers through the openings in a ring die. Granules are formed of a commercial size 4-6 mm in diameter and 15-20 mm long, allowing for their dispersion with a seeder.
Thermal treatment eliminates pathogenic organisms and contributes to surface hardness of the granules. The drying stage occurs in a drying cylinder. A device supplying hot air performs drying to 12-15% moisture content at 145-80°C. The finished product is blown with cold air for cooling and cleaning it from dust. The air supply device is equipped with a compressor and forcing and exhausting fans. An air separator cleans air from solid dust particles (the tiniest granule fraction). After that they are returned to the screw granulator.
Dry granules received from a hopper for the finished product are forwarded for packing in plastic bags by a filling machine. The quality of granules must meet the Ukrainian Standard Specifications TU U 20.1-36712791-001:2015 "Organic fertilizers based on poultry manure". The bags are delivered to a storehouse for the end products by a loader.

3. Conclusions

Based on the conducted research, it is found that the proposed composition of poultry manure with clinoptilolite and palygorskite mixture additives changes the quality indicators of agricultural soils in a positive way. Within 24 days the ammonium nitrogen content increased evenly in 4-6 times, the phosphorus content rose in 1.38-3.45 times, and the potassium, calcium and mangan content remained almost unchanged as compared to the background. Taking into account the experimental data, it is determined that the highest mechanical hardness of granules of this composition dried at T = 140°C is 80 kg f/m^2 with moisture weight fraction – 30 %. Based on the conducted studies, we presented a process flow diagram for utilization of poultry manure and production of low-emission organic fertilizer of prolonged action on their basis. The proposed technology will provide for reduction of the power costs for production and the increased quality of the granules. At the same time, it ensures elimination of helminths and pathogens.

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