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# DETERMINING THE OPTIMAL RATIO OF NATURAL MINERAL ADSORBENTS WITH REGARD TO AMMONIA ADSORPTION

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***Purpose***. Research on an impact of ambient temperature on ammonia adsorption from poultry droppings with the mix of clinoptilolite and palygorskite, and determination of their optimum ratio. ***Methodology***. There has been patent research carried out in the field of the objective. The laboratory-analytical phase involved determination of the ammonia concentration by a standard (titrated) solution of sulphur acid, and back titration of surplus acid by a standard solution of sodium hydroxide with present methyl red. ***Results.*** of the conducted research prove the effectiveness of ammonia absorption by mixtures of clinoptilolite and palygorskite in different proportions under temperature within 10 to $25^0$ C. ***Originality.*** Sorption mechanisms and rate depend on the pore structure and configuration. Increased adsorption capacity can be achieved by combination of features of crystal and clay minerals. In the author's opinion, the main part of this target component concentrated on the top of the laminate-stripe structure of palygorskite due to the surface diffusion. As to clinoptilolite, which features a framework structure, ammonia molecules fill the pore volume due to in internal molecular diffusion and are kept in the field of adsorption forces. ***Practical value.*** Of adding a composition of palygorskite from Dashukivka Deposit and clinoptilolite from Sokyrnytsia Deposit in even portions to the poultry manure would facilitate the efficient moisture reduction to the granulation phase as well as ammonia fixation. This would allow decreasing the nitrogen loss during storage of an organic-mineral fertilizer and contribute to the reduced air pollution with ammonia. *References 12, no tables, figures 4.*
**Key words**: ammonia, ecological safety, ecological danger, palygorskite, clinoptilolite, adsorption.

# ВИЗНАЧЕННЯ ОПТИМАЛЬНОГО СПІВВІДНОШЕННЯ ПРИРОДНИХ МІНЕРАЛЬНИХ АДСОРБЕНТІВ ЩОДО ПОГЛИНАННЯ АМІАКУ

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Досліджено перспективність використання палигорскита Дашукивского родовища і кліноптилоліту Сокирницького родовища для виробництва органо-мінерального добрива. Внесення цих дисперсних сорбентів в курячий послід сприятиме ефективному зниженню вологи до початку етапу грануляції, а також адсорбції аміаку з посліду. Це допоможе закріпити азот в обмінній формі і зменшити його втрату. Проведено експериментальні дослідження для визначення оптимальної пропорції суміші природних мінеральних сорбентів з поглинання аміаку. Встановлено, що найкраще процес поглинання відбувається в разі температури повітряного середовища 20°С. Оптимальне співвідношення сорбентів становить 1:1 (5 г кліноптилоліту : 5г палигорскита). Тоді маса адсорбованого аміаку досягає 8,17×10-2 г NH3 /10 г сорбенту. Результати досліджень будуть використані для розробки принципової схеми ефективної утилізації курячого посліду.
**Ключові слова:** аміак, екологічна безпека,екологічна небезпека, палигорськіт, клиноптилоліт, адсорбція.

**PROBLEM STATEMENT.** The current agricultural sector involves up to 30% of basic production assets, producing over 20% of the gross social product and forming 70% of retail sales. Territorial spread of the agricultural sector is the largest as compared to the other industries of Ukraine. An impact of agricultural production on the environment rises because of mechanization causing overconsolidation of plough and subsurface horizons, excessive plowing of lands, land-reclamation operations carried out without proper reasoning, and soil chemicalization.

Development and implementation of highly effective science-based activities on preservation of the land resources and enhancement of soil fertility are of great importance.

According to the existing technology, poultry used for meat production is kept on permanent litter 3 to

10 cm thick. Based on the regulations [1], litter demand for broiler stock is 1.5 kg per chicken. Usually litter is made of haulm from cereals (rye, wheat, barley), husk, chaffed stems of sunflower and peat (or fragmented peat), and rarely of wood shavings and sawdust. The main emphasis is put of water absorbability, safety of the material for nestling and an ability to utilize litter further as a fertilizer. Specialists do not recommend using sawdust and sunflower husk as litter, because very small litter particles can be pecked by chicken resulting in obstruction of the digestive tract. Before laying the litter, the floor is recommended to be covered with powdered lime in the amount of 0.5 kg/m$^2$ (lime is a disinfecting agent against pathogenic organisms and moisture adsorbent [1, 2]).

After poultry slaughter, litter is removed, kept at a dung-yard or allocated land plot (unorganized source of ammonia emission), and may be composted within one month and sold (taken away to fields as an organic fertilizer). Poultry droppings are as effective as mineral fertilizers; however, due to their organic form, nutrients are much less washed away from soil, well taken up by roots and do not result in high salt concentration. An assimilable form of nitrogen amounts up to 50%, phosphorus up to 20% and potassium up to 70%. The main periods for applying manure are spring and autumn with the basic till, though it is helpful to do nourishment during the whole plant vegetation.

In fertilization with chicken manure, there is a risk of burns of the plant's root system, resulting in growth inhibition and death of a plant.

Further, this type of a fertilizer will provide favorable conditions for the plants growth and yielding capacity increase, as well as reduction of the soil acidity.

Based on an analysis of the existing publications we can outline the following problematic stages:

1. ammonia emanation directly in a facility where chicken are kept;
2. storage of unprocessed/processed droppings of a different moisture content for a long period at a dung-yard;
3. carrying out operations of milling, granulation, disinfection and mechanical and thermal dehydration of droppings.

Nevertheless, improvement of those methods and development of more effective and environment-friendly ones is an up-to day research and practice task. The primary shortcomings of the existing processes are inability to make a product in a form, suitable for storage and further application, and multi-operational preparation of the raw product.

Let's take a detailed look at specifics of each of the stages.

1. Chicken droppings during their accumulation in a poultry house or a storage place for disposed litter are a source of emission of noxious gases into the atmosphere, affecting the health of chicken and service staff, as well as the environment in the poultry farm influence area. According to the norms of poultry house process design [2], ammonia release from 1 m$^2$ of litter is 25mg/h, hydrogen sulphide release is 15 mg/h and carbonic acid gas release is 8 mg/h.

There are researches carried out on the decrease of gas contamination inside of a poultry house. [3, 9] provide an analysis of the existing litter processing methods (chemical, physicochemical, biological), used to reduce contamination with pathogenic microorganisms and emission of harmful gases, and deodorize foul smell in premises. [10, 11] suggest using a mix of clinoptilolite tuff (30% - 60%) and montmorillonite (5% - 60%) or a mix of clinoptilolite tuff (30% - 60%), montmorillonite (5% - 60% of a total tuff weight) and bentonite clay (10% - 50% of a total mix weight) as a litter material. Lack of this method is relatively high outlay of natural disperse sorbents and uncomfortable living conditions for nestlings.

We propose raising chickens on "classic litter", composing of chicken droppings, chopped wheat straw and thin-ground floured CaO. Calcium oxide is of alkali nature, and its presence in an organic-mineral fertilizer would have a favourable effect on pH of agricultural soils, which usually are sub-acid. Water absorbability of straw (as compared to turf or zeolite) is worse. Based on a crop type, storage and a milling degree, water absorption occurs differently. Usually, one-year straw is preferred. Milling of 20 cm straw to 2.5-5 cm increases its water absorbability 1.5-5 times [3]. In addition, milled straw would make the droppings milling and granulation operations easier to make it suitable for storage and further use.

2. Fresh chicken droppings refers to the Hazard Category III, having strongly pronounced smell. During storage at a dung-yard as well as rotting through and fermentation, droppings emit into the atmosphere gases with foul specific smell like ammonia, hydrogen sulphide, carbon dioxide, sulphur dioxide and mercaptans. Additionally, when storing chicken droppings at a dung-yard pure, their loss may be by organic substance up to 30%, by nitrogen up to 36%, by phosphorous up to 12% and potassium up to 10%. A primary way to preserve nutrients in chicken droppings for a long-term period is composting using natural sorbents. For this purpose, they are to be mixed or laid layer-by-layer with one of the following components (total weight %): turf (25% - 30%), straw (15% - 20%), sawdust (30% - 50%). Composting duration depends on the product requirements. The organic fertilizer occurs within 3 to 6 months, while pure humus requires over 6 months. However, native manure has negative physical and mechanical characteristics, as it is not crumbly, sticky, and difficult to handle, package and evenly distribute for the nourishment purposes. The product becomes the most valuable when it is thermally dried (though during drying, the drying agent is contaminated with ammonia and other compounds, and hence the content of these compounds in the product drops).

3. Poultry manure without drying may contain the remains of pathogenic flora and harmful maggots. Therefore, optimal from the economical point of view droppings processing lines are to be developed to produce granulated organic-mineral fertilizers [4, 5, 6, 7, 8] as to mechanical and thermal dehydration, which would also provide additional disinfection against pathogenic microorganisms.

There are three technological methods to increase the grain quality: pelleting the fertilizer grains with inert materials (e.g. sulphur); encapsulating the fertilizer grains with polymer coating; and introducing nitrogen to the compounds with relatively low solubility. This would ensure a long-term effect on soils and plants due to even distributions of nutrients [12].

The objective of this research was to determine an optimum ratio of components in the mixture of natural mineral sorbents as to the absorption of ammonia containing in droppings.

**EXPERIMENTAL PART AND RESULTS OBTAINED.** The experimental studies have been conducted using the litter mix from a poultry farm, composing of chicken droppings, chopped wheat straw and thin-ground floured CaO. The adsorbents used were clinoptilolite from Sokyrnytsia Deposit and palygorskite from Dashukivka Deposit. Sorbent samples for the tests were prepared of a disperse composition, meeting the recommended one for practical application in the field of vegetation and farming: 0.5-1.0 mm. The sorbents were pre-dried at 105°C for 1 hour in order to remove physical water and increase the porosity.

A diagram of the testing laboratory plant used for the study is shown in the Figure 1. It comprises of a reaction flask (2), connected to an air pump Atinan At-A850 (1) and a Drechsel flask (3). The reaction flask of 50 $dm^3$ contained a droppings mixture (4) with sorbents (5) in a certain proportion and 1 ml of $NH_4OH$ (25%).

The modeling mixtures were held for 1 hour. The previous studies have shown that the time period of 30 minutes is sufficient to achieve the balanced ammonia concentration between the sorbent and the flask's air space.

Then we poured 150 ml of distilled water, 10 ml of $H_2SO_4$ (0.5M) and 6 drops of methyl red into the Drechsel flask. After reaching the working conditions in the plant, we observed the absorption of the balanced remainder of the ammonia concentration from the ammonia-air mix by the reaction solution. After certain time intervals (5, 10, 15, 30, 60, 120, 180 min.) the Drechsel flask was replaced with another one and the selected sample was titrated using NaOH (1M). The ammonia weight absorbed by the sorbents was calculated based on the study results.

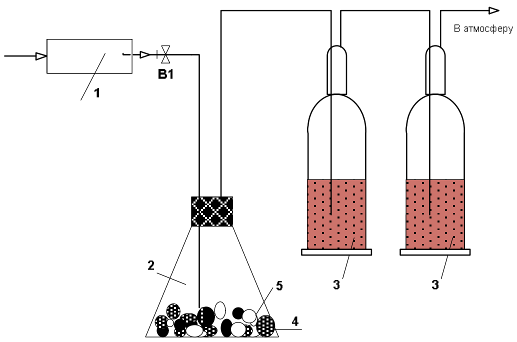


Figure 1 – Diagram of the laboratory plant

Adsorption is an exothermal process; hence, reduced medium temperature should facilitate the process of ammonia absorption. An impact of the ambient temperature on the adsorption capacity of clinoptilolite and palygorskite in respect of ammonia was determined experimentally.

The results are shown in the Figures 2 and 3.

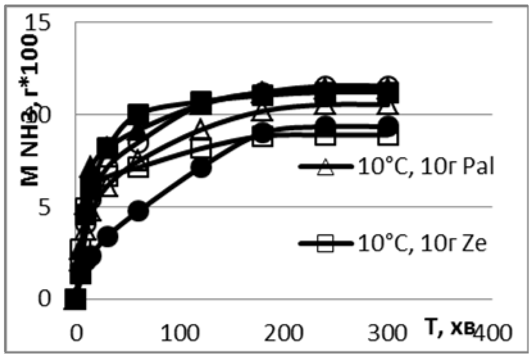


Figure 2 – Effectiveness of ammonia absorption from an air-gas flow with mineral sorbents at temperatures of $10^0$ and $15^0$C

Experimental data indicate that the absorption process occurs in the best way under the air temperature of 20°C. Also, the experimental data show that the ambient temperature within 10-25°C does not influence significantly the adsorption process; therefore, further experiments were carried out within this ambient temperature range.

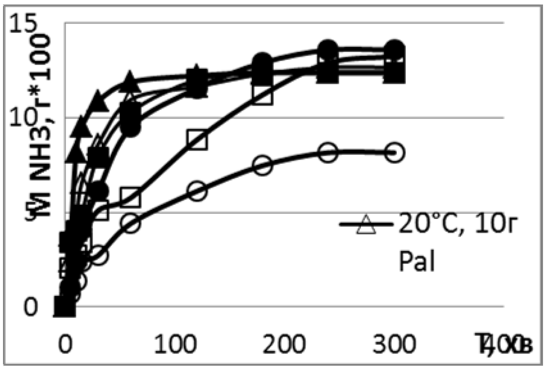


Figure 3 – Effectiveness of ammonia absorption from the air-gas flow with mineral sorbents at temperatures $20^0$ and $25^0$C.

Due to the crystal structure, clinoptilolite is more heat-stable and acid-resistance than palygorskite. At the same time, palygorskite, which structure is laminated, has better adsorption capacity as to coarse molecules. Palygorskite features high absorbability on account of zeolite channels of 0.37x0.64 μm and 0.56x1.10 μm (primary pores), which are located in crystals and form part of the stripe. Sometimes the stripes are strongly combined, creating pores of various forms 200 to 300 μm in length with the average cross-section of 0.27 μm (secondary pores). However, low physical strength may restrict practical application of this clay sorbent as a litter material.

Our further step was to determine an optimum ratio in order to achieve a set of necessary properties of both sorbents. For this purpose, we prepared batches in the following proportions: 0:10 g of clinoptilolite; 0:10 g of palygorskite; 1.5:8.5; 3:7; 5:5; 7:3; 8.5:1.5 g of the sorbents. Studies have been conducted by the above methods and under isothermal conditions (T=20°C). Temperature mode of the process has been kept constant using a thermostat. The results are shown in the Figure 4. An analysis of the results suggests that the highest capacity has been shown by a composition in the proportion of 1:1 (5 g of clinoptilolite: 5 g of palygorskite).

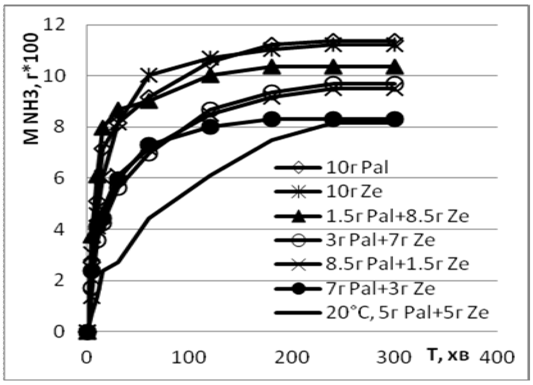


Figure 4 – Effectiveness of ammonia absorption from the air-gas flow with mineral sorbents of different component ratios

The adsorption process consists of three stages: diffusion of molecules of the occluded substance from the flow to the outside surface of sorbent grains – outside diffusion; diffusion of molecules of the occluded substance inside of sorbent grains – inside diffusion; holding absorbed molecules in the area of adsorbing forces. Such high results can be explained by the “double” ion-exchange adsorption. For palygorskite it is typical for exchangeable ions to stay at the edges and ribs of the crystals (on the mineral’s top). Free inter-crystal volume of clinoptilolite makes 0.34 of the total volume of this macroporous sorbent with the relatively low specific surface.

**CONCLUSIONS.** The conducted research allows affirming the prospects of combined application of palygorskite from Dashukivka Deposit and clinoptilolite from Sokyrnytsia Deposit for ammonia absorption from the air-gas flow of droppings ventilation with further use as an organic-mineral fertilizer of a prolonged action. This would allow reducing the environmental hazard of air pollution with nitrogen, disposing droppings from a poultry farm, contributing to reduced nitrogen loss during storage and increasing soil fertility.

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# ОПРЕДЕЛЕНИЕ ОПТИМАЛЬНОГО СООТНОШЕНИЯ ПРИРОДНЫХ МИНЕРАЛЬНЫХ АДСОРБЕНТОВ ПО ПОГЛОЩЕНИЮ АММИАКА

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Исследована перспективность использования палигорскита Дашукивского месторождения и клиноптилолита Сокирницкого месторождения для производства органо-минерального удобрения. Внесение этих дисперсных сорбентов в куриный помет будет способствовать эффективному снижению влаги до начала этапа грануляции, а также адсорбции аммиака из помета. Это поможет закрепить азот в обменной форме и уменьшить его потерю. Проведены экспериментальные исследования для определения оптимальной пропорции смеси природных минеральных сорбентов по поглощению аммиака. Установлено, что лучше всего процесс поглощения происходит в случае температуры воздушной среды 20°С. Оптимальное соотношение сорбентов составляет 1:1 (5 г клиноптилолита : 5г палигорскита). Тогда масса адсорбированного аммиака достигает $8,17 \times 10^{-2}$ г $NH_3$ /10 г сорбента. Результаты исследований будут использованы для разработки принципиальной схемы эффективной утилизации куриного помета.

**Ключевые слова:** аммиак, экологическая опасность, экологическая безопасность, палигорскит, клиноптилолит, адсорбция.