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THE SYNTHESIS OF PROLONGED FERTILIZERS BY MEANS OF ADSORPTION OF NUTRITION AND TRACE ELEMENTS BY NATURAL SORBENTS FROM INDUSTRIAL AND AGRICULTURAL WASTES

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Annotation. *Are investigated the optimal conditions for absorption of ammonia from airborne gas flow ventilation of chicken excrements with the usage of mixture of natural sorbents. The resulting product can be used in the future as organic fertilizers of prolonged action. Are studied the optimal conditions of adsorption of zinc ions from industrial wastes by bentonite, using the resulting product as a carrier of trace elements in fertilizers.*

Key words: ***ammonia, chicken excrements, natural sorbents, zinc ions, fertilizers of prolonged action***

Utilization of industrial and agricultural wastes, which often contain compounds of ammonium, phosphorus, potassium, calcium, sulfur, heavy metals requires the use of sophisticated technologies, searching the ways of recycling of concentrated and localized compounds of these pollutions, and therefore additional investments. However, these compounds could be used in the case of selective extraction of contaminated liquid or solid wastes as nutrition or trace elements in agroengineering, providing by this the increase in crop yields and the improvement in crop quality. Such possibility of extraction of separate nutrition or trace elements appears in the case of usage of natural sorbents in waste treatment technologies that are inexpensive, effective adsorbents. This helps to prevent the compounds pollution of the environment and at the same time to get a product that can be effectively used in agricultural technologies.

The most common contaminants of agricultural wastes are ammonium compounds, which are accompanying the vital activity of livestock and poultry. Their usage in concentrated form in agricultural technologies is related with the risk of overdose and creating of negative impact on the vital activity of agricultural plants. Adsorption on the sorbents allows getting the effective prolonged fertilizers, applying of sorbents in soil can at the same time improve their structure and adsorption capacity.

In accordance with the existing technology, the poultry which is used for meat production is held in constant litter with the thickness of 3–10 cm. According to regulations [1, 2] the need in litter for chicken broilers is 1,5kh/ poultry unit. For bedding is typically used cereals straw (rye, wheat, barley), husk and crushed sunflower stalks, peat (or peat crumb), more rarely - wood shavings and sawdust with the addition of lime. The studies concerning the way to reduce the gas concentration in poultry house room are conducting. In [3–9] is provided an analysis of existing methods for treatment of bedding materials (chemical, physical- chemical, biological) that are carried out to reduce their contamination with pathogens, emission of harmful gases and deodorization of odors in the room. In [10, 11] is proposed to use as bedding material the mixture of clinoptilolite tuff (30% – 60%) and montmorillonite (5% – 60%) or the mixture of clinoptilolite tuff (30% – 60%) and montmorillonite (5% – 60%) of the total mass of tuff and bentonite clay (10% to 50%) of the total weight of the mixture. The disadvantage of this method is a relatively high cost of natural dispersed sorbents and the creation of uncomfortable living conditions for the chicks. We propose to grow up chickens on the "classic litter", which consists of chicken excrements, chopped wheat straw and grounded CaO. Due to the shredding of straw with 20cm in length to the size of 2.5–5 cm, the moisture-absorbing capacity increases in 1,5–5 times [3].

One of the important trace elements, necessary for the ensuring of vital activity of plants is zinc. This element has a great influence on the oxidizing-renewable processes, the speed of which is perceptibly reduced with its shortage: a violation of hydrocarbon conversion processes takes a place. It was established that with the shortage of zinc in the leaves and roots of tomato, citrus and other crops, are accumulating phenolic compounds, phytosterols or lecithins, and is reduced the starch content. It was found out that large doses of phosphorus and nitrogen reinforce the signs of deficiency of zinc in plants and that the zinc fertilizer is particularly necessary when applying high doses of phosphorus and nitrogen. Zinc affects the synthesis of sucrose, starch, total content of carbohydrates and proteins. The application of zinc fertilizer increases the amount of ascorbic acid, dry matter and chlorophyll. Zinc can be applied as adsorbed on natural sorbents from liquid industrial wastes ions.

The aim of the research. The aim of research was to establish the optimal conditions of adsorption of ammonium compounds and zinc ions in natural sorbents to obtain effective prolonged fertilizers.

Material and methods of research. For obtaining prolonged ammonium fertilizer we used a mixture of poultry litter, which consisted of chicken

excrements, chopped wheat straw and grounded CaO. As adsorbents were used clinoptilolite from Sokyrnytskyi deposit and palygorskite from Cherkassy deposit. For experiments were prepared samples of sorbents with dispersion composition that correspond to that recommended for practical application in crop and animal production: 0.5–1.0 mm. Sorbents were dried in advance at the temperature 105°C for 1 hour, that contributed to physical removal of water and increased porosity. The scheme of experimental laboratory plant, on which the study was conducted, is shown in Figure 1. It consists of the reaction flask (2), to which is joined the air pump Atinan At-A850 (1) and Drexel cup (3). In the reaction flask with holding capacity of 50 dm^3 was placed a mixture of excrements (4) with sorbents (5) in a certain proportion and 1 mL of NH4OH (25%). Model mixtures were kept for 1 hour. Previous studies have found that the time period of 30 minutes is sufficient to establish the equilibrium concentration of ammonia in sorbent and the air space bulb.

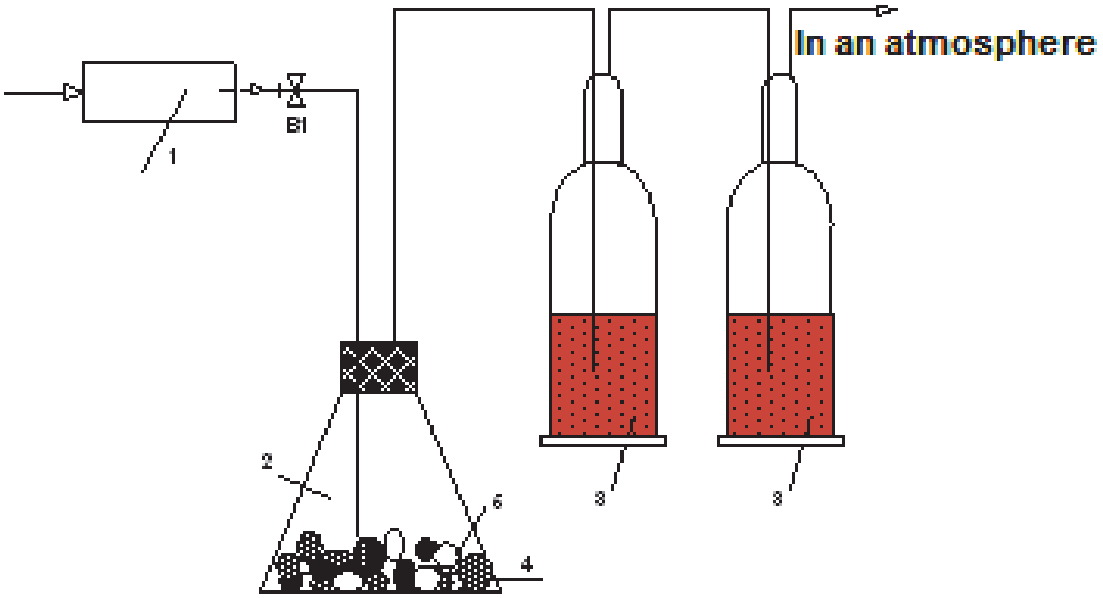

Fig. 1. The scheme of laboratory plant

In Drexel glass was poured 150 ml of distilled water, 10 ml of H2SO4 (0.5m), 6 drops of methyl red. After setting up the mode of installation of plant the absorption of equilibrium residual concentration of ammonia from ammonia-air mixture by the reaction solution has happened. At the regular intervals (5, 10, 15, 30, 60, 120, 180hv) Drexel glass was changed into another; the selected sample was titrated by NaOH (1N). The mass of ammonia absorbed by sorbent was calculated on the basis of research results.

During the research we have determined the optimal ratio required for the receiving of necessary properties of both sorbents. For this batches were prepared in mass 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 sorbents. The research was conducted by the method described above and isothermal conditions (T = 20°C). Constant temperature conditions of the process were supported via thermostat.

The research of zinc sorption in natural sorbents was carried out in thermostatic apparatus with stirrer in periodic and continuous mode of its rotation. As sorbent was used bentonite of second productive layer from Dashukivskiy career of Cherkasy region, at the dosage of sorbent 5 ÷ 20 g/ dm^3. The mineral composition of bentonite is the following: the second horizon is represented mainly by montmorillonite (70-95%) and impurities of fine calcite and quartz. The research methodology of adsorption of zinc ions from industrial wastes lies in the following: constant operating temperature 20 °C was achieved in the thermostat and was subsequently maintained. In the flask, placed in a thermostat, a batch of bentonite was carried in, and then was poured in the prepared solution with a given concentration of zinc ions. Thereafter the stirrer was turned on, the shaft of which rotated with a fixed frequency that was determined via the regulator. After some time the hashing process was stopped, samples were filtered out using the filter paper "blue ribbon", the filtrate was analyzed for the contents of zinc ions by standard methods.

Results of the research. The results of studies concerning the determination of optimum ratio for receiving the complex of required properties of both sorbents are presented in Fig. 2. The analysis of the research indicates that the composition in ratio 1:1 (5g of clinoptilolite: 5g of palygorskite) demonstrated the highest capacity.

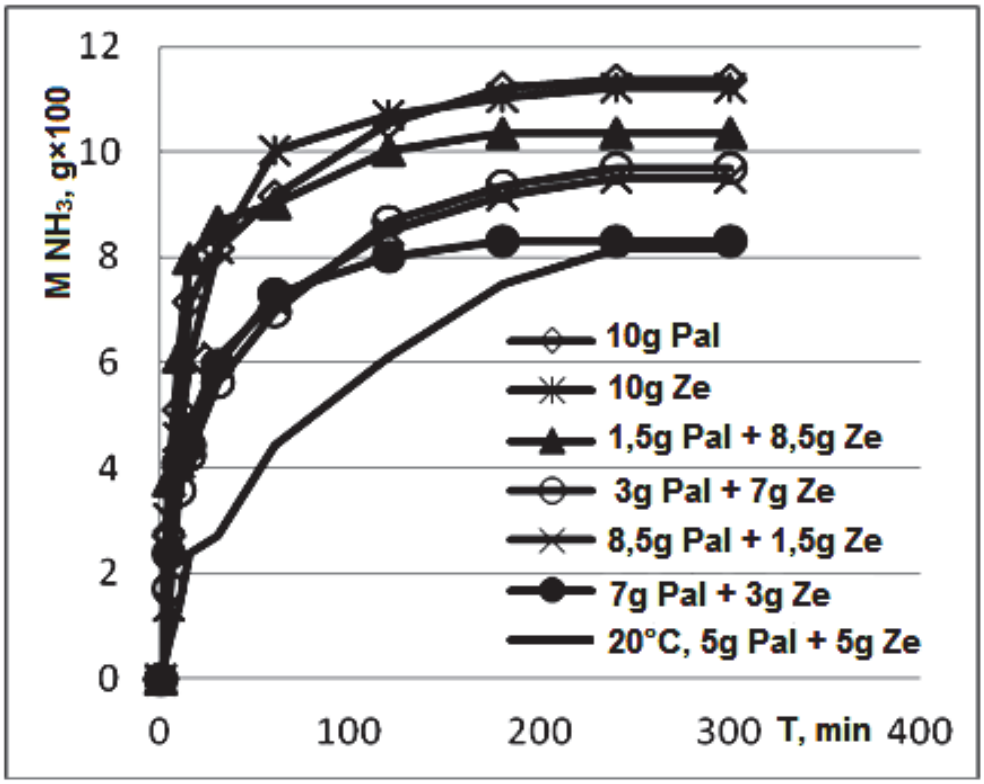

Fig. 2. The efficiency of absorption of ammonia from airborne gas flow by mineral sorbents with different ratios of components

The adsorption process involves three stages: the diffusion of molecules of sorbed substance from flow to the outer surface of the sorbent grains-external diffusion; the diffusion of molecules of sorbed substance inside the grains of absorber-internal diffusion; the retention of absorbed molecules in the field of adsorption forces. These good results can be explained by "double" ion-exchange adsorption. For palygorskite the existence of ion exchange on the ends and edges of the crystals (on the surface of the mineral) is typical. Free internally crystalline volume of clinoptilolite is 0.34 of the total volume of the macroporous sorbent with a relatively low specific surface.

Kinetics of adsorption of zinc ions from the liquid industry wastes is presented in Fig. 3. The concentration of the original solution was 500 mg/ L, the amount of sorbent dosage was 5 g. The operating temperature of the experiment was 20 °C; the adsorption process duration varied from 1 hour to 12 hours. Sampling and analysis of samples was carried out hourly.

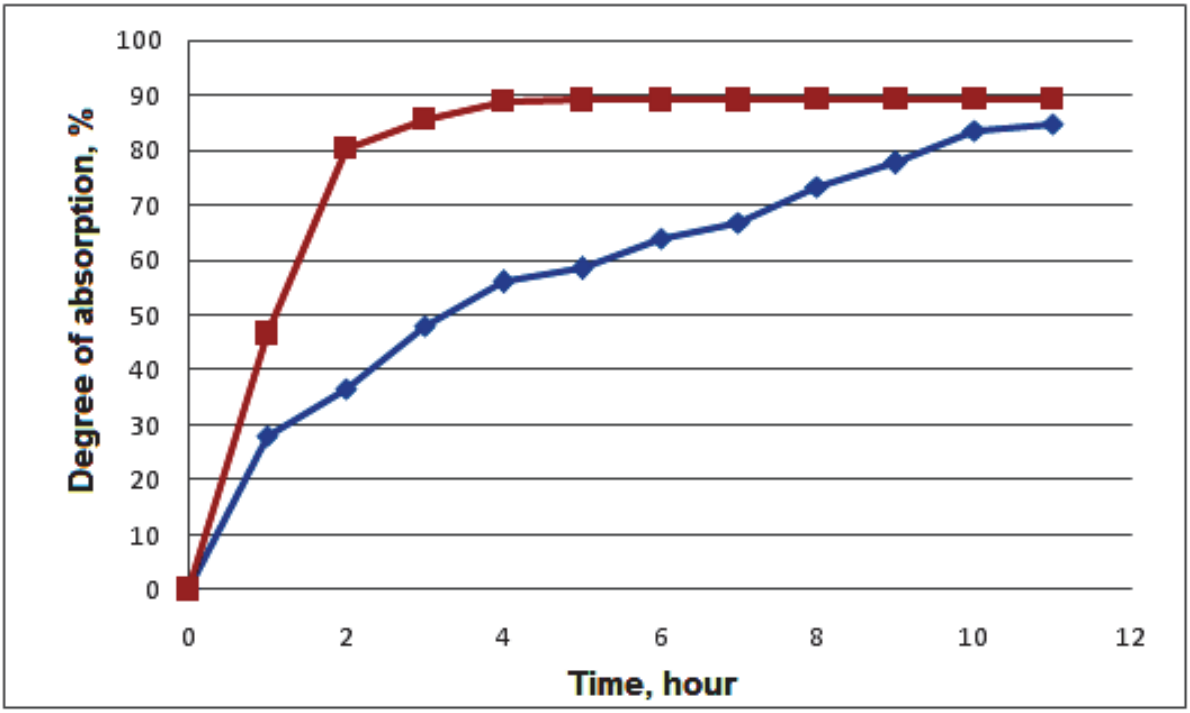

Fig. 3. Kinetics of zinc ions (II) adsorption in the time interval 0-12 hours under mixing conditions: —■— periodic; —♦— constant.

Generally, the results of the conducted experiments showed that the maximum zinc ions absorption occurs within 24 hours under periodic mixing conditions; and the value of residual concentrations practically doesn't change after 6 hours of mixing under constant mixing conditions. Maximum absorption occurs within 0.5–7 hours; but when the concentration of zinc ions in the flows is less than 500 mg / l, the adsorption process is more steady over time. In the case of increasing of zinc ions concentration, the adsorption efficiency is reduced because there is saturation (filling) of the mineral surface by adsorbate that confirms superficial character of sorption.

The next stage of the study was to establish the amount (dose) effect of adsorbent on a depth of sorption flow. As it is shown from Fig. 4 and exponential relationships, adsorption efficiency increases when the dose of adsorbent also increases, due to an increase in the surface, where the sorption is.

It is necessary to note the functional backlog of specific adsorption growth from the adsorbent weight increasing, indicating, mostly the superficial sorption. Such parameter as adsorbent dose can not be universally measured by these dependencies. When taking into account the quality of the waste water composition, the initial and desired final concentration of pollutants in the aqueous phase, the amount of bentonite spent for cleaning, it can be varied, but the reasonable rate is 5...12.5 g / dm3 at metal ions concentration 500 mg / dm3, and the increasing of the dose over a specified value is ineffective. [12]

To install the technologically rational values of such parameter as dose powdered sorbent, we united the dependence of specific absorption and cleaning efficiency on the amount of adsorbent. The intersection of these curves will give a rational value of dosage sorbent amount. As it is shown in Fig. 5, a reasonable dose is 5–8 g of sorbent per 1 dm^3 of flows (under condition that the initial concentration of pollutants does not exceed 1000 mg / dm3). At higher zinc ions concentrations, it is appropriate to increase the sorbent dosage to 10 g.

Conclusions. The conducted studies suggest the prospects of applying a clinoptilolite mixture of Sokyrnytsky deposits and palygorskite of Dashukivsky deposit for absorption of ammonia from air and gas flow ventilation of chicken manure with the following usage as organic fertilizers of prolonged action. This will reduce the ecological danger of environmental pollution by ammonia nitrogen, utilize the poultry litter, reduce nitrogen losses during storage and increase soil fertility.

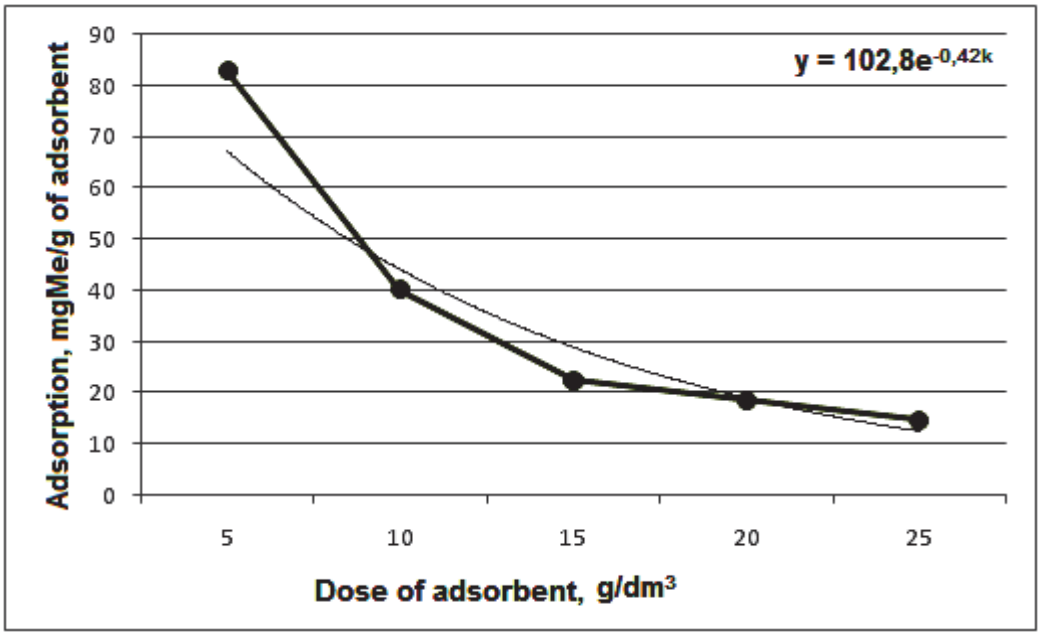

Fig. 4. Dependence of specific adsorption of zinc ions from the sorbent dose

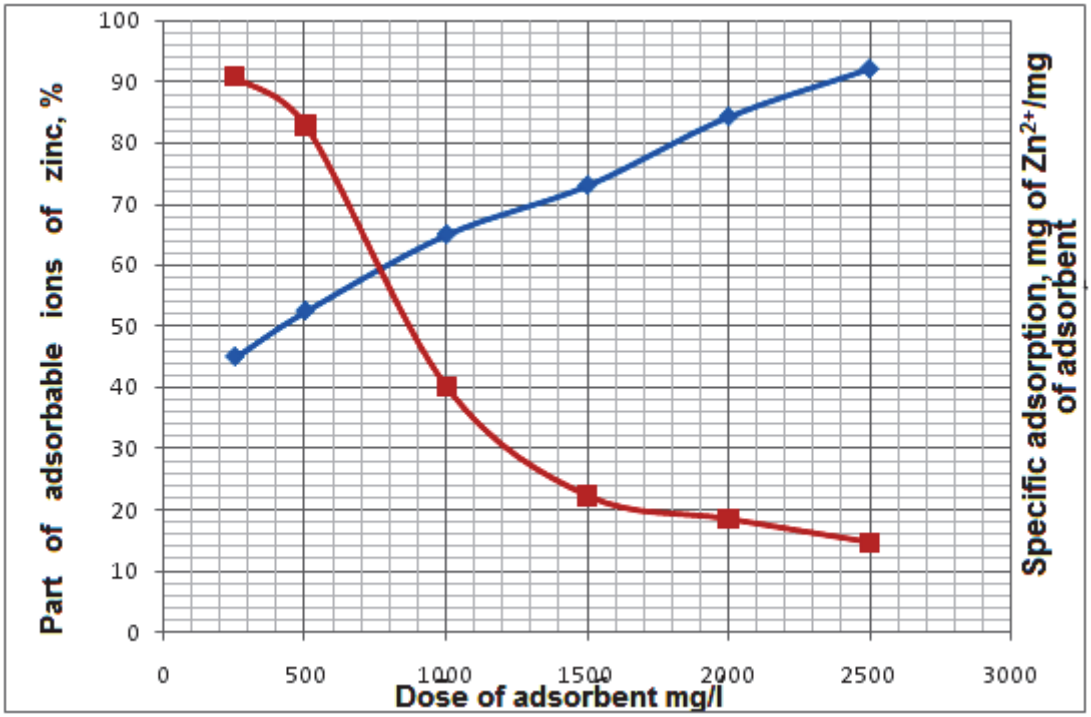

Fig. 5. Rational adsorbent dose for the zinc ions absorption from an aqueous environment (- ■ - specific adsorption; - ♦ - adsorption efficiency)

It is experimentally proved that the maximum zinc ions absorption occurs within 30 minutes and practically full after 24 hours. The degree of wastewater contaminants at different concentrations and dosage amounts of the sorbent were determined. The rational dose is 5-8 g of bentonite per 1 dm^3 of waste (under condition that the initial concentration of pollutants does not exceed 1000 mg / dm3). The resulting adsorbent with adsorbed zinc ions can be used as a carrier of microelements in fertilizers.

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СИНТЕЗ ПРОЛОНГОВАНИХ ДОБРИВ ШЛЯХОМ АДСОРБЦІЇ ЕЛЕМЕНТІВ ЖИВЛЕННЯ ТА МІКРОЕЛЕМЕНТІВ ПРИРОДНИМИ СОРБЕНТАМИ З ПРОМИСЛОВИХ ТА СІЛЬСЬКОГОСПОДАРСЬКИХ ВІДХОДІВ

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Анотація. *Досліджено оптимальні умови поглинання аміаку з повітряно-газового потоку вентилювання курячого посліду з використанням суміші природних сорбентів. Отриманий продукт може використовуватися в подальшому як органо-мінеральне добриво пролонгованої дії. Досліджено оптимальні умови адсорбції іонів цинку з промислових відходів бентонітом із використанням отриманого продукту як носія мікроелементів у мінеральних добривах.*

Ключові слова: ***аміак, курячий послід, природні сорбенти, іони цинку, добрива пролонгованої дії***

СИНТЕЗ ПРОЛОНГИРОВАННЫХ УДОБРЕНИЙ ПУТЕМ АДСОРБЦИИ ЭЛЕМЕНТОВ ПИТАНИЯ И МИКРОЭЛЕМЕНТОВ ПРИРОДНЫМ СОРБЕНТОМ ИЗ ПРОМЫШЛЕННЫХ И СЕЛЬСКОХОЗЯЙСТВЕННЫХ ОТХОДОВ

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Аннотация. *Исследованы оптимальные условия поглощения аммиака с воздушно-газового потока вентилирования куриного помета с использованием смеси природных сорбентов. Полученный продукт может использоваться в дальнейшем как органо-минеральное удобрение пролонгированного действия. Исследованы оптимальные условия адсорбции ионов цинка из промышленных отходов бентонитом с использованием полученного продукта как носителя микроэлементов в минеральных удобрениях.*

Ключевые слова: ***аммиак, куриный помет, естественные сорбенты, ионы цинка, удобрения пролонгированного действия***