Chemical and analytical properties of zeolite-containing rocks, poultry farm waste and their composite mixtures

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Abstract. The comparative mineral composition of the zeolite-containing rock of the Terbunskoye field, poultry farm waste and composite mixtures with poultry farm waste has been carried out. The authors investigated the chemical and analytical properties of 3 variants of composite mixtures in relation to the waste of a poultry farm: zeolite - 45:55; 90:55; 180: 55. The method of spectrophotometry was the first to determine the chemical properties of zeolite samples and composite mixtures - antioxidant activity (inhibition of 0.025% DPPH solution, λ-517nm) in aqueous and alcoholic (carbinol) extracts; the sum of phenolic compounds (by the Folin-Chocalteu method, λ-750), and absorption spectra in the UV and visible spectral regions. The content of the main nutrients - Na, Mg, P, K Ca, Zn and Mo in the waste samples of the poultry farm is 15; 6, 21; 3.6; 14; 5.5 and 3.9 times higher, respectively, then in zeolite samples. And the use of composite mixtures contributes to the creation of fertilizers with specified parameters in terms of mineral composition.

1. Introduction

Poultry farming is actively developing in most countries of the world, as it is the basis of life support for many people, regardless of income level [1]. Organic waste that accumulates in large quantities near poultry farms is very harmful to the environment.

The use of poultry manure as fertilizer can provide yields comparable to commercial fertilizers, but long-term use at high application rates can reduce pasture productivity due to nutrient oversupply [2,3]. Therefore, it is necessary to manage the continuous land use of poultry manure to minimize the potential impact on the environment [4].

In this aspect, it is relevant to use poultry waste together with natural zeolites.

Zeolites are important materials with very wide applications in agriculture and environmental engineering. It has been established that the inclusion of zeolite in the soil increases the productivity of agricultural crops and increases the efficiency of nutrient use [5]. The adsorption properties of natural zeolite are widely known [6,7].

The introduction into agricultural production of new organomineral fertilizers based on agricultural waste with a high content of bioorganic components and highly efficient, nanoporous natural minerals with high sorption and detoxification activity is one of the priority directions in the development of environmentally friendly and resource-saving technologies.
Therefore, the purpose of our research was to study the mineral composition and chemical properties of zeolite samples, poultry farm waste and their composite mixtures to identify the best options for their further use in agriculture and plant growing.

2. Materials and methods
The research was carried out in 2019 on the basis of the research laboratory of YSU, I.A. Bunin and the scientific laboratory of the All-Russian Institute of Selection and Technology of Horticulture and Nursery of the Russian Agricultural Academy.

The object of the study was chicken litter droppings (sampling place - Svetlyi Put LLC, Kamenskoye village, Eletsky district, Lipetsk region), natural zeolite (sampling place - Kazinka village, Terbunsky district, Lipetsk region), as well as their mixtures in the following corresponding ratios - 45:55; 90:55 and 180:55.

To study the chemical-analytical and morphological properties of the zeolite-containing rock, poultry farm waste and composite mixtures based on them, the electron microscopic method was used, the dispersion of zeolite samples was 2.5-0.25 mm. For this, an analytical scanning electron microscope (SEM) EVO LA 15 (Seis, Germany) was used.

The chemical properties of zeolite samples and composite mixtures were determined for the first time by spectrophotometry: antioxidant activity (inhibition of 0.025% DPPH solution, \(\lambda\) = 517nm) in aqueous and alcoholic (carbinol) extracts; the sum of phenolic compounds (by the Folin-Cholcalteu method, \(\lambda\)-750), and absorption spectra in the UV and visible spectral regions.

3. Results and discussion
Zeolites consist of pores and angular aluminosilicate (AlO4 and SiO4) tetrahedra, connected in three-dimensional frames [8]. Therefore, to begin with, the pore size of the zeolite particles was investigated, which fluctuates from 360-270 nm (figure 1 A) to 760-530 nm (figure 1 B). It is in the volume of macro- micro and mesopores that the main absorption (sorption) occurs due to van der Waals forces of nonspecific interaction and it is their presence that will affect the filtration and transport properties of the zeolite-containing rock [9].

![Figure 1. Size and average number of pores in zeolite samples.](image-url)

Such a structure of nanoporous natural minerals will make it possible to retain in its framework the mineral elements contained in the waste.

Chemical analysis of the mineral composition showed that the average mineral composition of the zeolite (wt%): Na (0.1), Mg (0.9), Al (9.4), Si (21.3), P (0.4) , S (0.3), K (1.6), Ca (0.8), Fe (2.3), Cj (9.5), Ni (3.4), Cu (0.3), Zn (1.1), Mo (1.2).

The average mineral composition of poultry farm waste is (wt%): Na (1.5), Mg (5.4), Al (0.5), Si (2.8), P (8.7), S (0.9), K (5.9), Ca (11.9), Fe (0.8), Co (9.2), Ni (4.6), Cu (0.7), Zn (5.5), Mo (4.7).
The content of the main nutrients - Na, Mg, P, K Ca, Zn and Mo in the waste samples of the poultry farm in 15; 6, 21; 3.6; fourteen; 5.5 and 3.9 times, respectively, higher than in zeolite samples (table 1).

**Table 1.** Comparative mineral composition of the zeolite-containing rock of the Terbunskoye field and poultry farm waste, wt%.

| Element | Zeolite | Waste poultry farms |
|---------|---------|---------------------|
| O*      | 38.38   | 36.75               |
| Na      | 0.12    | 1.59                |
| Mg      | 0.91    | 5.89                |
| Al      | 9.40    | 0.41                |
| Si      | 21.33   | 2.94                |
| P       | 0.44    | 8.16                |
| S       | 0.23    | 0.94                |
| K       | 1.61    | 4.88                |
| Ca      | 0.75    | 10.21               |
| Cr      | 0.01    | 0.01                |
| Mn      | 0.31    | 0.01                |
| Fe      | 2.28    | 4.31                |
| Co      | 9.55    | 6.19                |
| Ni      | 3.36    | 3.04                |
| Cu      | 0.31    | 0.23                |
| Zn      | 1.02    | 2.76                |
| Mo      | 5.59    | 3.07                |

For the first time, the order of accumulation of 16 elements in samples of zeolite-containing rock from the Terbunskoye deposit and in waste from a poultry farm has been determined.

A decreasing number of elements in samples of a zeolite-containing rock:

Si>Al>Co>Mo>Ni>Fe>K>Zn>Mg>Ca>P> Mn>Cu>S>Na>Cr.

A decreasing number of elements in poultry waste samples:

Ca>P>Co>Mg>K<Fe< Ni<Mo>Zn>Si> Al>Cu>Mn> Na>S>Cr.

Differences in the component composition of elements in the composition of zeolite and poultry farm waste are shown in figures 2 and 3.

**Figure 2.** Mineral composition of zeolite.
Figure 3. Mineral composition of poultry waste.

The results of the EDS spectra showed that Si, O, Al, and Ca predominate in the composition of the zeolite. The bulk of the poultry waste is P, Mg, Ca.

We investigated the chemical and analytical properties of 3 variants of composite mixtures in relation to the waste of a poultry farm: zeolite - 45:55; 90: 55; 180: 55.

Depending on the composition of the composite mixture, the quantitative composition of the elements varies considerably (table 2).

Comprehensive management of six macronutrients: nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca) and magnesium (Mg), as well as seven trace elements - iron (Fe), manganese (Mn), zinc (Zn), boron (B), copper (Cu), molybdenum (Mo) and chloride (Cl) are those that most agronomists consider necessary only for sustainable crop yields [10].

Table 2. Comparative mineral composition of composite mixtures, wt%.

| Element | Test options (poultry waste: zeolite (%)) |
|---------|-----------------------------------------|
|         | 45:55 | 90:55 | 180 : 55 |
| O*      | 32.98 | 41.35 | 32.87    |
| Na      | 1.21  | 0.43  | 0.87     |
| Mg      | 3.98  | 1.26  | 1.72     |
| Al      | 5.81  | 7.09  | 6.09     |
| Si      | 8.84  | 16.71 | 14.26    |
| P       | 1.19  | 0.99  | 2.59     |
| S       | 1.69  | 0.17  | 0.17     |
| K       | 4.17  | 1.72  | 2.24     |
| Ca      | 1.71  | 0.97  | 3.61     |
| Cr      | 0.12  | 0.06  | 0.16     |
| Mn      | 0.28  | 0.05  | 0.39     |
| Fe      | 4.71  | 5.15  | 6.87     |
| Co      | 7.54  | 8.76  | 11.61    |
| Ni      | 3.12  | 3.41  | 4.28     |
| Cu      | 0.42  | 0.17  | 0.47     |
| Zn      | 2.42  | 1.41  | 2.42     |
| Mo      | 3.38  | 3.58  | 2.35     |
The research results showed that the obtained experimental mixtures were saturated at the expense of waste from poultry farms with the following important elements: P, K, Ca, Fe, Zn.

Using these ratios, it is possible to regulate the process of introducing microelements depending on their content in the soil by reducing the proportion of zeolite or waste in order to exclude their excess.

At the same time, the established high mineral composition of the finished organic-mineral fertilizer, the use of which will make it possible to obtain products enriched with microelements, which is very important in conditions of functional nutrition.

The chemical properties of zeolite samples and composite mixtures have been determined for the first time by spectrophotometry - antioxidant activity (inhibition of 0.025% DPPH solution, λ-517 nm) in aqueous and alcoholic (carbinol) extracts; the sum of phenolic compounds (by the Folin-Chocalteu method, λ-750), and absorption spectra in the UV and visible spectral regions. The high antioxidant activity of aqueous extracts and the sum of phenolic compounds of samples of poultry farm waste and mixtures based on them indicates the presence of soluble biologically active substances (table 3). The presence of antioxidant activity and phenolic compounds in zeolite samples indicates the presence of organic impurities. We assume that nutrients will be well absorbed by the porous structure of the zeolite, which will ensure their gradual release in the soil and good absorption by plants.

**Table 3.** Antioxidant activity and the sum of phenolic compounds of zeolite, poultry waste and composite mixtures based on them.

| Samples                        | Antioxidant activity,% | Sum of phenolic compounds, mg/g sample |
|--------------------------------|------------------------|----------------------------------------|
|                               | alcohol extraction     | water extraction                       |                                       |
| Zeolite                        | 2.94                   | 4.88                                   | 0.4                                   |
| Poultry waste                  | 8.15                   | 70.26                                  | 4.3                                   |
| Composite mixtures, zeolite: poultry waste |
| 45 : 55                        | 4.48                   | 23.49                                  | 1.2                                   |
| 90 : 55                        | 2.97                   | 39.05                                  | 2.7                                   |
| 180 : 55                       | 4.33                   | 47.08                                  | 3.5                                   |

Typical absorption spectra of aqueous and alcoholic extracts are shown in figure 4. Absorption in the range of 200-350 nm indicates the presence of biologically active compounds extracted by water. For the alcohol extract, the main absorption regions are 38-45 nm and 600-700 nm, which probably corresponds to high-molecular substances and pigments.

**Figure 4.** Absorption spectra of composite mixtures. On the left is an aqueous extract, on the right is an alcoholic extract.
4. Conclusion
Our comprehensive morphological and chemical studies of zeolite-containing rocks, composite mixtures with poultry farm waste confirm the expediency of using them as organo-mineral fertilizers in intensive farming and crop production technologies.

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