



IMPROVEMENT OF FERTILIZING PROPERTIES OF GLAUCONITE UNDER MICROWAVE RADIATION

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ABSTRACT

This work was conducted with the purpose of finding a method to increase the fertilizing properties of glauconite using a rectangular microwave resonant cavity. For the modified glauconite, we measured the specific surface area, the total porosity and the mean pore radius via Quanta chrome Instruments high-speed gas sorption analyzer NOVA series 1200e. The equilibrium concentrations of heavy metal ions in solutions were measured using X-ray fluorescence on Shimadzu EDX-7000/8000 energy dispersive X-ray fluorescence spectrometer. The statistical parameters of heavy metal ions adsorption from soil were obtained by building mathematically processed adsorption isotherms. The calibration curve of dependence was constructed in "A-C_{equil}" coordinates. Biogenic cations were determined by the spectrometric analysis. The fertilizing properties of glauconite were verified through the cultivation of peas. Electromagnetic radiation of super high frequency with 3 kW power and 2150-2450 MHz frequency is shown to be applicable for the non-thermal modification of glauconite, increasing the performance properties of this mineral while using it as a crops fertilizer. The optimum treatment regime was selected, according to which glauconite should be exposed to radiation for 5 minutes. We found out that this method allows improving physical, adsorptive, cation-exchange and fertilizing properties of the ore, especially in concentrated form. Glauconite, modified by electromagnetic radiation of super high frequency, when contacting soil, promotes the increase of potassium, calcium and magnesium cations in it. At the same time, the level of heavy metals - iron, manganese and copper decreases due to their adsorption by soil particles. This glauconite proved to be a highly effective full-fledged fertilizer, stimulating, first of all, the development of the root system of peas, as well as above-ground parts of the plant. In comparative experiments with untreated and modified by electromagnetic radiation of super high frequency glauconite, in the first case the length of the main root in comparison with the not fertilized control increased by 32%, the height of the green mass - by 24%; under modified glauconite, the root and green mass increased by 35.3% and 63.4% respectively. The received results are important for more rational usage of glauconite in agriculture and show perspective in applying the modified by microwave radiation concentrated form of glauconite as a fertilizer for legume and other cultures.

Keywords: glauconite, microwave radiation, non-thermal modification, adsorption, ion-exchange and physical properties, stimulation of the growth of peas.

INTRODUCTION

Conventional mineral and organic fertilizers are not environmentally friendly. At that point, the priority, in our opinion, belongs to local ores, primarily glauconite.

Glauconite is a well-known valuable ore as it contains a number of major and trace elements [3, 12]. In addition, it has a unique crystal lattice and microcrystalline pores. Being used in agriculture, especially in regions with arid climate, glauconite due to such structure provides high ion-exchange, selective and absorbing capacity. This improves the physicochemical and biological properties of the soil, as well as the state of the environment through the adsorption of heavy metals [1].

Water adsorbed in the pores of glauconite is an efficient additional supply of soil moisture, available for plants. It doesn't evaporate and doesn't move to the underlying soil horizons. This is especially valuable for soils with a reduced water capacity and insufficient moisture in zones with hard and unpredictable weather conditions [2]. All of the above explains the creation of

various fertilizers for agriculture on the basis of glauconite [15, 17-21].

However, a significant obstacle to the widespread use of glauconite ore is the insufficiently expressed fertilizing properties and the low concentration of glauconite itself. This circumstance increases the expenses on transportation and insertion of the aforementioned ore [14, 22].

Given the above, the purpose of this work was to find a way to improve the fertilizing properties of glauconite. We assumed that one of such methods would be the use of microwave radiation, which has been successfully applied in various fields. Thus, electromagnetic radiation of super high frequency is widely used in the manufacturing industry for heat treatment of various materials (drying, sterilization, pasteurization, etc.) [9, 25, 27]. It is considered promising to use microwave radiation in the chemical industry, too [26]. At the same time, in the available literature, we haven't found any information on the application of microwave radiation in agriculture. Compared with the



standard types of treatment, microwave radiation has a number of advantages, such as volumetric impact on the material and high processing speed [7, 11]. Such an advantage as high controllability of the microwave radiation process is achieved due to the possibility of an easy and smooth (and, if necessary, sharp) alteration of the power of the radiation source [13, 23].

The tasks of the present studies included: the study of the effect of microwave radiation on the porosity of glauconite, its specific surface area and average pore radius under the different periods of exposure to microwave treatment; the impact of modified concentrated glauconite on the cations content level in soil; the study of parameters of heavy metal ions adsorption by glauconite; measuring the effectiveness of using treated with microwave radiation glauconite in vegetative experiments.

MATERIAL AND METHODS

The experiment on determining the influence of microwave treatment on the physical properties of glauconite sand and its concentrate was carried out according to the following scheme: 1) glauconite sand without microwave treatment; 2) concentrated glauconite without microwave treatment; 3) glauconite sand with microwave treatment for 2.5 minutes; 4) concentrated glauconite with microwave treatment for 2.5 minutes; 5) glauconite sand with microwave treatment for 5 minutes; 6) concentrated glauconite with microwave treatment for 5 minutes; 7) glauconite sand with microwave treatment for 10 minutes; 8) concentrated glauconite with microwave treatment for 10 minutes.

A rectangular resonant cavity was used to conduct the microwave treatment of glauconite. The power of the radiation source was 3 kW, and the frequency was 2150-2450 MHz. There was an additional microwave power absorber in the resonant cavity, which made it possible to change the distribution of the electromagnetic field in the resonant cavity and, accordingly, in the heated sample.

When using the microwave electromagnetic field, measuring the temperature of the sample in the working cavity becomes difficult; because of this, time intervals were used.

In the course of the work, we studied samples of glauconite sand from the pit of the Belozerskoye Field, located in Lysogorsky District, Saratov Oblast, and glauconite concentrate obtained using a special technology by the method of dry magnetic separation. The weight of the samples was 400 g. For concentrated glauconite samples, the specific surface area, total porosity and mean pore radius were investigated. The measurements were carried out on a Quantachrome Instruments high-speed gas sorption analyzer NOVA series 1200e.

In the experiments, the chestnut medium-thick low-humus soil was used. In the arable layer, this soil contains 2.2% humus. The sum of the absorbed bases is 31.8 meq per 100 g of soil, pH is 8.4. The soil isn't saline. The availability of hydrolysable nitrogen is medium, mobile phosphorus - weak, exchangeable potassium - high for all crops.

To calculate the static parameters of adsorption of heavy metal ions, the method of constructing and subsequent mathematical processing of adsorption isotherms was applied. To plot the curves, 1 g of each studied soil samples was placed in 100 ml solutions of heavy metal salts (Fe^{+2} , Mg^{+2} , Cu^{+2}) with given initial concentrations in the range from 10 to 1000 mg/l. The control was commercial adsorbents Birm and Greensand. All samples were stirred intermittently. The contact time of the sorbents with solutions was 3 hours. After that, the equilibrium concentrations of ions in solutions were measured by constructing the calibration curve of dependence in "A- C_{equil} " coordinates. To make the above measurements, the method of X-ray fluorescence was used and performed on Shimadzu EDX-7000/8000 energy dispersive X-ray fluorescence spectrometer. The value A was calculated from the formula:

$$A = (C_0 - C_{\text{equil}}) \frac{V}{m} \quad (1)$$

where A - adsorption of the determined ion, mg/g, C_0 and C_{equil} - initial and equilibrium concentrations of ions in solution, mg/l; V is the volume of the solution, l; m - sorbent weight, g.

To determine the content of K^+ , Ca^{+2} , Mg^{+2} cations in soil samples; firstly we measured their gross content before insertion of glauconite. The same cations were determined on the 10th day after glauconite was added in an amount of 12 wt%. The measurement was carried out by a spectrometric method.

Potassium, calcium and magnesium were chosen for study among other chemical elements due to their important role in the life of plants. It is well known that they all are biogenic, being part of the composition of a plant. For example, potassium maintains complete balance and takes part in the hydration of cell colloids, providing in the latter metabolic processes due to the functioning of a large number of enzymes. In addition, this chemical element increases the resistance of plants to various unfavorable conditions, such as short-term drought, low temperatures and various diseases.

In contrast to potassium, calcium is involved in the development of the root system. It promotes the intake of nutrients in the plant organism. At the same time, it inhibits the penetration of heavy metals.

Magnesium, like potassium, actively participates in metabolic processes, like an activator of a number of enzymes. It is also necessary for the photosynthetic process, being part of the chlorophyll composition.

Vegetative experiments in order to determine the influence of microwave radiation on the fertilizing properties of glauconite were carried out according to the following scheme: 1) control; 2) glauconite sand without microwave treatment; 3) concentrated glauconite without microwave treatment; 4) glauconite sand with microwave treatment for 5 minutes; 5) concentrated glauconite with microwave treatment for 5 minutes.



This experiment was conducted according to the standard method, in vegetation vessels with the dimensions of 23.5×16.5×18.5 cm. The experiment was replicated six times. The dosage of glauconite insertion was 10 g per vessel. The object of this experiment was peas cultivar 'Flagman 12'; we measured the height of the plants and of length of the main roots after 15 days of vegetation.

RESULTS

The obtained results are presented in Tables 1 and 2 and in the Figure. As follows from Table-1, an increase in glauconite concentration from 35 to 70% contributed to a slight growth in the specific surface area of the ore. However, when processing the concentrated and initial samples with microwave radiation for 2.5 min, the specific surface area index increased by 21.1 and 20.2 m²/g, respectively, or by 45.2 and 41.9%, respectively. The increase in the duration of microwave radiation of samples

up to 5 min led to a further growth of this index by 34.0 and 34.9 m²/g, or by 72.8 and 72.4%, respectively (Table-1). When glauconite samples were irradiated for 10 min, the specific surface area index changed insignificantly compared with the 5-minute treatment. As for porosity of investigated glauconite samples, it was slightly higher in concentrated glauconite before it was treated by microwave radiation. After treatment for 2.5 minutes, this index increased in comparison with the initial state by 0.149 for concentrated and 0.065 cm³/g for initial glauconite, or by 126.9 and 52.4%, respectively. When the samples were exposed to microwave radiation for 5 minutes, the porosity increased additionally only for concentrated glauconite by 0.165 cm³/g, or by 133%. A further increase in the time of exposure to microwave radiation for glauconite samples resulted in the increase in porosity by 0.183 and 0.187 cm³/g, which made up 155.1 and 151.0%, respectively.

Table-1. Effect of microwave radiation on the physical properties of glauconite sand and its concentrate.

No.	Sample	Specific surface area, m ² /g	Porosity, cm ³ /g	Mean pore radius, nm
1	Glauconite sand without microwave treatment	46.7	0.118	23.5
2	Concentrated glauconite without microwave treatment	48.2	0.124	25.0
3	Glauconite sand treated with microwave radiation for 2.5 minutes	67.8	0.267	16.4
4	Concentrated glauconite treated with microwave radiation for 2.5 minutes	68.4	0.189	16.9
5	Glauconite sand treated with microwave radiation for 5 minutes	80.7	0.182	28.1
6	Concentrated glauconite treated with microwave radiation for 5 minutes	83.1	0.289	28.9
7	Glauconite sand treated with microwave radiation for 10 minutes	81.3	0.301	17.3
8	Concentrated glauconite treated with microwave radiation for 10 minutes	85.8	0.311	18.4

Microwave radiation also affected the mean radius of the pores. In the initial state, this index differed a little between studied samples. However, after treating them for 2.5 minutes it decreased to 16.4 and 16.9 nm. With a 5-minute irradiation, a significant increase in the pore radius was observed. An interesting fact in our experiment was that a 10-minute microwave radiation treatment led to the reduction of this index to the level reached by irradiation for 2.5 minutes (Table-1).

When studying the influence of concentrated glauconite treated with microwave radiation on the content of potassium, magnesium and calcium cations in the soil, a significant and positive effect was registered. When 10 days after insertion passed, the content of these elements increased by 0.4, 0.10 and 0.4% respectively, or 1.22-1.35 times. In the greatest degree, this was established for magnesium and potassium cations, and to a lesser extent, for calcium cation (Table-2).

Table-2. Influence of concentrated glauconite treated with microwave radiation on cation content in soil.

Name of cations	Cations content, %	
	Before insertion	10 days after insertion
K ⁺	1.5	1.9
Mg ⁺²	0.28	0.38
Ca ⁺²	1.8	2.2

The most important property of glauconite, as is known, is its ability to adsorb heavy metals while contacting with soil. This is extremely important from environmental point of view. However, in this respect a poorly understood issue is the effect that glauconite treated with microwave radiation has on this process. Therefore, in our work we carried out relevant research. The results obtained are shown in Figures (1-3) in the form of



adsorption isotherms of heavy metals with the given initial concentrations.

The studied samples of concentrated glauconite, especially the one treated with microwave radiation,

adsorbed all metals more intensively than commercial adsorbents. This property was most clearly manifested for copper and iron and less significantly for manganese (Figures 1-3).

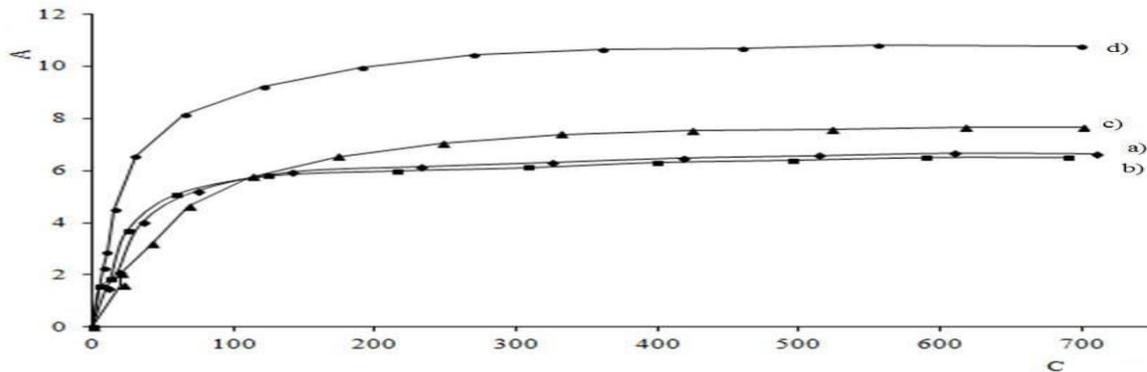


Figure-1. Isotherms of adsorption of iron (1), manganese (2) and copper (3). Legend: (a - Birm, b - Greensand, c - concentrated glauconite without treatment, d - concentrated glauconite after microwave radiation).

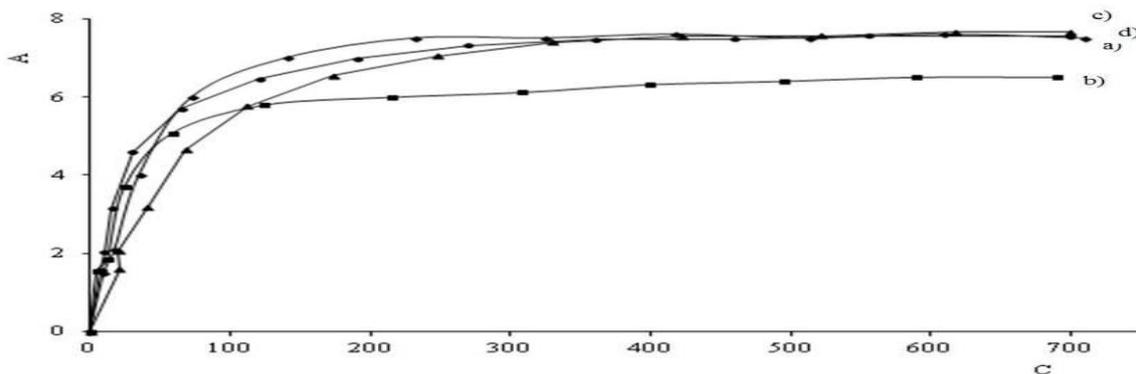


Figure-2. Isotherms of adsorption of iron (1), manganese (2) and copper (3). Legend: (a - Birm, b - Greensand, c - concentrated glauconite without treatment, d - concentrated glauconite after microwave radiation).

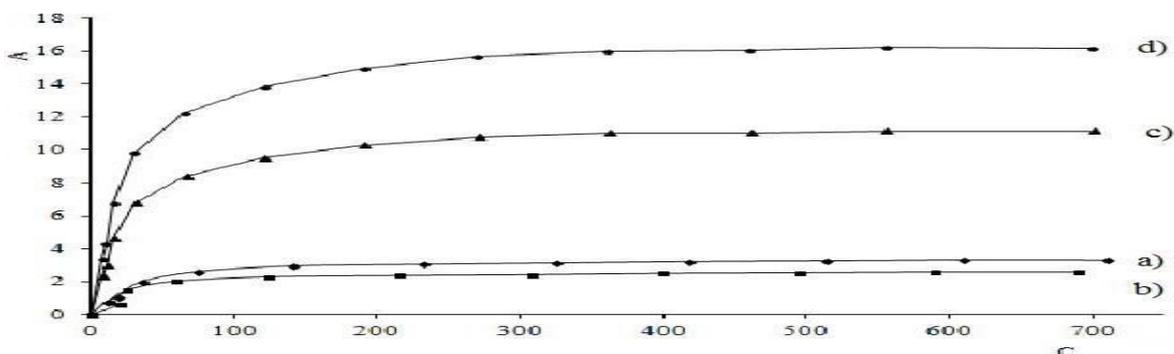


Figure-3. Isotherms of adsorption of iron (1), manganese (2) and copper (3). Legend: (a - Birm, b - Greensand, c - concentrated glauconite without treatment, d - concentrated glauconite after microwave radiation).

In the course of the vegetative experiments, it was found that concentrated glauconite acted like a full-fledged fertilizer, primarily stimulating the development of the root system in peas, as well as its above-ground parts. Glauconite treated with microwave radiation contributed to this process to a greater extent. After the use of non-

treated glauconite, the height of plants increased by 24.2%, and the length of the main root - by 32%, compared with the control. Glauconite irradiation allowed to increase these values to 35.3 and 63.4%, respectively.



DISCUSSIONS

In the present paper, the results of studying the properties of glauconite originated from the Belozerskoye Field, located in Lysogorsky District, Saratov Oblast, and modified with electromagnetic radiation of super high frequency, are presented.

Glauconite sand has a number of properties that allow it to be used both as sorbents and as a fertilizer. However, its value is significantly reduced by the presence of barren in it [4, 10]. The sorption properties, as revealed earlier, can be increased by thermal activation [6]. In our work, it was also shown that microwave treatment positively influenced the physical characteristics of glauconite. Its specific surface area increased somewhat after concentration, but this happened much stronger after microwave irradiation of the ore and its concentrate. The dependence of the duration of electromagnetic field influence on the studied properties of glauconite is revealed. The maximum effect was obtained after 5-minute irradiation.

This time interval positively affected the increase in the size of the pores and their mean radius. Such physical modification of glauconite enhanced its adsorption and cation-exchange properties. It is known that the molecular adsorption of this ore is associated with the infiltration of electrolyte solutions into the free spaces of the crystal structure and the sorption of anions and cations from solutions of electrolytes that are in aqueous solutions, including soil solutions [8]. An interesting fact obtained in the present study was observed in the soil increase of potassium, magnesium and calcium cations, which are necessary for plants, with the simultaneous glauconite adsorption of heavy metals (iron, manganese and copper). This was manifested to the greatest degree in modified by microwave radiation concentrated glauconite. It was also found by Russian authors that glauconite concentrates from the Bondarskoye and Karinskoe Fields quite effectively sorbed magnesium, iron, lead, copper, etc. [5, 24], while foreign authors used other adsorbents for these purposes [28-32].

In the available literature, we didn't find any information about the positive effect of glauconite modified by microwave radiation on the growth and development of plants. As was claimed by the present studies, its insertion into the soil had a positive effect on the growth of the root and green parts of the peas, i.e. it showed itself as a sufficiently effective fertilizer.

CONCLUSIONS

It was found that the fertilizing properties of glauconite sand and, especially, its concentrated form, increase significantly when it is modified by microwave radiation with a power of 3 kW and of 2150-2450 MHz frequency. At the same time, the specific surface area, porosity and mean pore radius of glauconite increased, especially with a 5-minute exposure.

It was revealed that while soil contacted with glauconite treated with microwave radiation, the content of the studied cations K^+ , Mg^{+2} , and Ca^{+2} increased 1.22-1.35 times in comparison with the control sample.

Microwave treatment of glauconite enhanced the adsorption of heavy metals, such as iron, manganese and copper. Concentrated and, especially, treated by microwave radiation glauconite has proved to be a highly effective full-fledged fertilizer, stimulating, above all, growth of the root system in peas plants.

In the future, we plan to conduct studies on the use of concentrated glauconite treated with microwave radiation for 5 minutes, on other crops, including vegetables, in the field. We also plan to use a complex organo-mineral fertilizer obtained on the basis of modified glauconite [16] with the study of the effect of this fertilizer on the nutrient regime and biological activity of the soil, yield and product quality.

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