

Efficiency of action of natural minerals at emission of greenhouse gases in substratum of dung

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The purpose. To determine efficiency of natural minerals at emission of greenhouse gases in dung substratum of cows under mesophilic conditions of anaerobic fermentation (in vitro). **Methods.** Researches are lead with the use of chemical, analytical and mathematical-statistical methods. They maintained fixed temperature for each stage of metagenesis (hydrolysis, oxidation, acetogenesis, metanogenesis) at mesophilic regimen of fermentation in the probed material and monitored the pH level of the medium. In experiment the probed substratum was intensely mixed by shaking containers. In dung mass of cows they determined acidity by means of pH-meter Tur N5170 (Poland). In the probed substratum they determined the level of carbonic gas by N.V. Chibisova technique, and CH₄ — by calculation method. **Results.** On the basis of the lead researches it is fixed that importation into the probed substratum of natural minerals — vermiculite, pearlite and zeolite — increases enzymatic activity of cow dung on 9; 7 and 6% accordingly in comparison to control (dung without preparations). Natural mineral glauconite (in vitro) reduces the level of CO₂ and CH₄ on 5% in dung substratum as compared to the control. **Conclusions.** Experimentally it is proved that more effective impact on metanogenesis process was application of vermiculite which increases evolution of carbonic gas and methane in cow dung, at the same time natural mineral glauconite deactivates fermentation and selection of greenhouse gases and consequently, glauconite can be used as means for decreasing blow out of greenhouse gases.

Key words: *dung, greenhouse gases, methane, carbonic gas, cows, natural minerals, metanogenesis.*

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The problem of preservation the environment from the pollution wastes of agro-industrial complex (AIC) and other branches of agriculture is an important task for all regions of Ukraine [1, 2]. The main reason of ecological problems of present time is the increase in the concentration of greenhouse gases in the atmosphere, that are formed as a result of anthropogenic activity and causes negative changes in the climate balance of the planet, namely: lead to an rise in temperature, droughts, floods, decrease of supplies of potable water and acid rain etc. [3–5]. For providing stable ecological development it is important retention of balance between absorption and greenhouse gas emissions. Taking into account the danger origin of a greenhouse effect at the global level, a number of necessary measures that would contribute the preservation of the natural environment is accepted [3]. Signing of the Paris Agreement which are aimed for the reduction the level of greenhouse gas emissions and limiting growth temperature of air to 2°C became the most powerful a step.

One of the main sources of greenhouse gases is agriculture, that on volume their emissions, though is inferior power engineering and industry, but is a powerful source of pollution, both in Ukraine and at global level [2, 6, 7]. According to literary data it is known that more than 52 million tons of manure per year receive from of the animals kept by enterprises AIC [8, 9]. The accumulation of livestock wastes creates a number of problems that decreases the efficiency of conduct agriculture, since they become a significant sources of environmental pollution [5, 9].

An important aspect in the functioning of agro-industrial enterprises is remained the processing of wastes livestock with minimal damage for a natural environment [1, 8]. One of the most perspective, ecologically safe and energy-efficient direction of decision this problem there is the use of organic wastes of livestock objects as alternative sources of energy, in particular receiving to the biogas, that contributes to improving the energy providing of separate regions by methane anaerobic fermentation of manure [1, 4–5, 7–8, 10].

Biogas is formed as a result of decomposition by bacteria of organic substrate that can be used, as natural gas and an additional source of energy, fuel and biofertilizer [9, 10]. Consequently, the process utilization of wastes of the agro-industrial complex, in particular manure contributes to a complex decision of energy, ecological and food problems [1, 8]. Due to the production of biogas by biological conversion of manure, takes place decrease of selection into the natural environment of the most important greenhouse gas a methane as one with of the best ways to prevent processes of global warming [11, 12]. Since it is known that methane influences on the greenhouse effect 21 times stronger than CO₂ and able to remain in an atmosphere to 12 years of age and also in 23 times more intensive of absorbs infrared radiation that contributes to creating a greenhouse effect [11]. Consequently, a production of biogas is effective and investment-attractive technology that is predetermine by the presence of significant raw material potential and low level of prime price of this type of energy [1, 7].

Taking into account the above, an important scientific and practical task is expansion of assortment of effective means for the processing of organic wastes of livestock complexes, that would give an opportunity to increase volumes production of additional energy resource of biogas, thus providing minimization of negative influences and consequences on the environment.

Materials and methods. The research was conducted in the laboratory of ecology of the Institute of agriculture of Carpathian region NAAS. Manure samples for determination of the amount of carbon dioxide and methane in the investigated substrate (in vitro) were taken in SE "RF «Obroshyne»", where the herd of Ukrainian black-and-white dairy cattle of the western intra-breed type is kept. In the experiment, methane forming raw material (manure) was presented in triple repeated in such variants: I variant – control (manure without the introduction of preparation), II variant – with the introduction of mineral the glauconite, 9 g; III variant – with the use of mineral the vermiculite, 40 g; IV – with the introduction of perlite, 30 g; V – with the use of mineral the zeolite, 6 g.

The process of methane fermentation was conducted in laboratory conditions (in vitro), using the flasks closed by stoppers to maintain tightness and providing of anaerobic conditions. Biomass (manure of cattle) was introduced into an experimental a capacity diluted with water in correlation of 1:1. In the process of research on every stage of methagenesis (hydrolysis, oxidation, acetogenesis, methanogenesis) at the mesophilic regime of fermentation in the investigated material the temperature regime was supported and control after the level of pH of the environment was carried out. During an experiment conducted mixing of the investigated substrate by intensive shaking of the capacities. Analogical conditions the process of methanogenesis were as in the control variant, where the anaerobic fermentation of the substrate was due to the natural manure microflora, as and in the experimental of analogues with the use of natural minerals.

In the manure mass of cows, acidity was determined using a pH-Meter Type N5170 (production of Poland). In the investigated substrate, conducted determination of the level of carbon dioxide out in accordance with the method of N. Chibisova [13], and CH₄ – by the calculation method.

The obtained digital material was worked by the method of variation statistics with the help the package of applications *Microsoft EXCEL* and *AtteStat*.

Research results. The process of methanogenesis was carried at optimal indicators fermentation in accordance with the method of V. Shatskyy, O. Sklyar, R. Sklyar [14]. The intensity of the process of anaerobic fermentation of organic wastes depends on the optimal conditions, on the creation of that is influences by a number of factors. One of the substantial parameters that influence the fermentative activity and the rate of reproduction of microorganisms and synthesis by them of biogas is the temperature regime [10, 15]. The process of methanogenesis can proceed in a wide range of temperatures and begins at t 6°C, since as known that at lower temperature of methane emissions ceases [10]. The study was carried out in a mesophilic regime fermentation of temperature within the limits of 25–33°C was supported.

On stability of the process of methanogenesis the reaction of the nutritious environment (pH) has considerable influence. Analyzing the hydrogen indicator during the fermentation, the oscillation of its values within the limits of 6,6–7,8 discovered, that indicates a sufficient level of acidity for the development of bacteria. Since it is known that the most intensive formation of biogas takes place at the values of pH, near to neutral, while at pH below 6,5 the activity of bacteria decreases, the output of biogas gets worse on 30–

40 % and at 6,0 the development of methane microflora is almost completely inhibited [15]. In subsequent researches, after introducing into the manure substrate of natural minerals an increase of pH from 7,8 to 9,0 during 23 days was noted, indicating the activation of the fermentative activity of biomass.

One of the important parameters of methane fermentation is also the time of the process of fermentation of biomass (exposition of fermentation). In most cases, at the processing of organic wastes the process of methanogenesis occurs during a 22–28 days and depends on a temperature regime [15]. In our experiment, the exposition of anaerobic fermentation with the aim of receipt of biogas was in the recommended limits and was 23 days.

The obtained results in the process of the research in the laboratory conditions (in vitro) with the introduction of natural minerals to the manure substrate are presented in the indicate below figures (Fig. 1, 2).

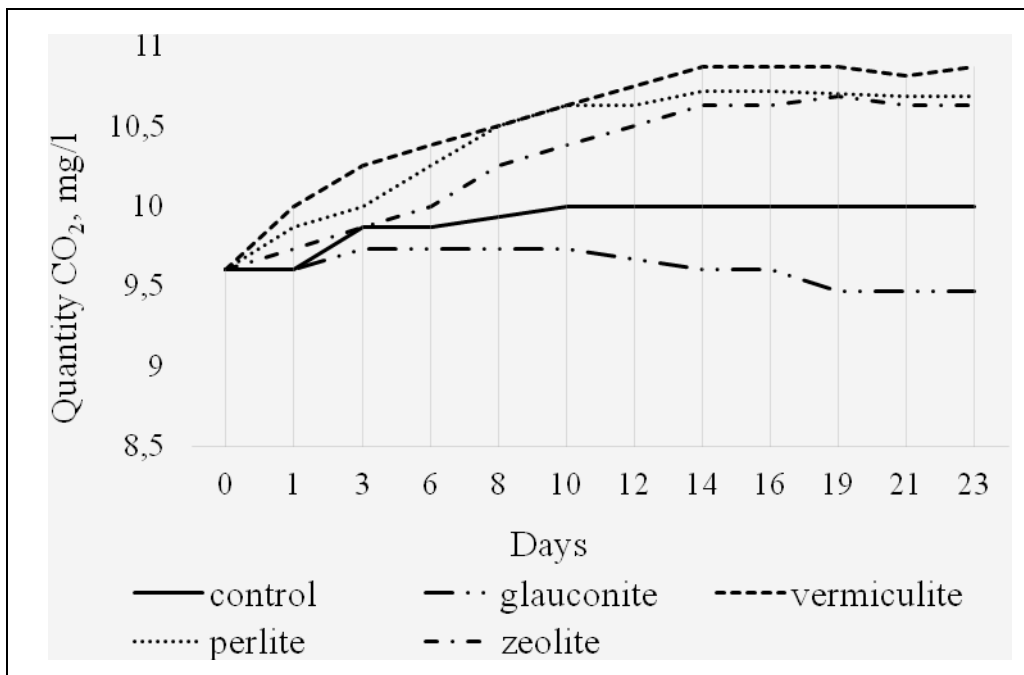


Fig. 1 – Quantity of carbon dioxide selected in variants using of natural minerals

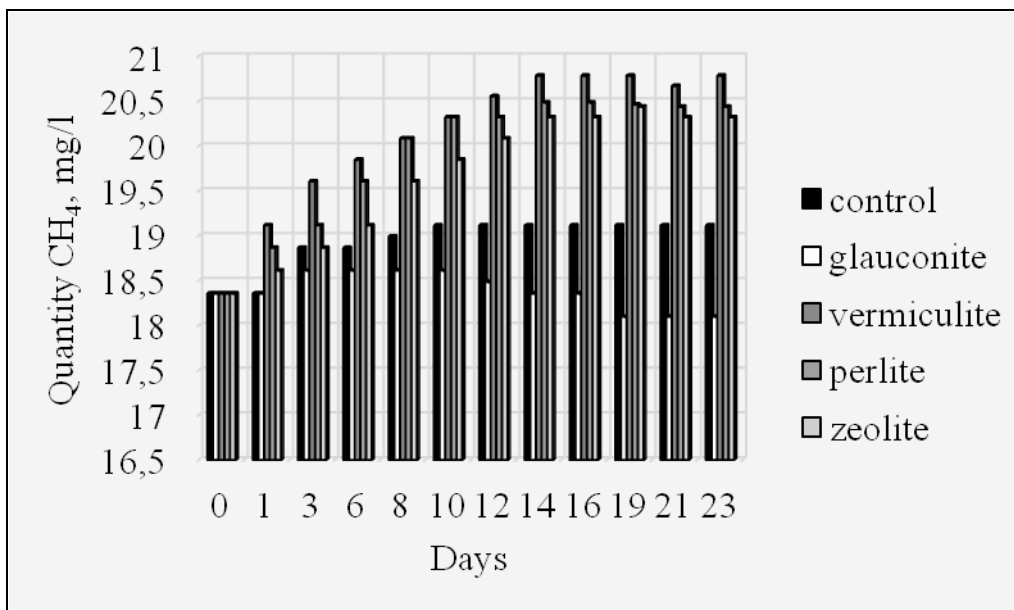


Fig. 2 – Quantity of methane selected in variants using of natural minerals

Analysis the results of experimental researches testifies that the use of natural minerals in the investigated material, except the mineral a glauconite causes an increase the output of CO₂ and CH₄ due to the rise in the activity of the process of anaerobic fermentation of biomass.

Tables 1 and 2 show the results of statistical processing of the allocation of CO₂ and CH₄ in the control and experimental samples.

Table 1 - Number of carbon dioxide isolated during methanogenesis, mg / l

| Days | Control | Glauconite | Vermiculite | Perlite | Zeolite |
|------|-----------|-------------|--------------|--------------|-------------|
| 1 | 9,60±0,02 | 9,60±0,16 | 9,99±0,15 | 9,87±0,08* | 9,73±0,10 |
| 3 | 9,87±0,02 | 9,73±0,08 | 10,3±0,07** | 9,99±0,13 | 9,87±0,11 |
| 6 | 9,87±0,04 | 9,73±0,21 | 10,4±0,11* | 10,3±0,15 | 9,99±0,09 |
| 8 | 9,93±0,04 | 9,73±0,10 | 10,5±0,19* | 10,5±0,07** | 10,3±0,09* |
| 10 | 9,99±0,05 | 9,73±0,20 | 10,6±0,14* | 10,6±0,12** | 10,4±0,06** |
| 12 | 9,99±0,03 | 9,67±0,24 | 10,8±0,15** | 10,6±0,09** | 10,5±0,08** |
| 14 | 9,99±0,02 | 9,60±0,08** | 10,9±0,24* | 10,7±0,05*** | 10,6±0,09** |
| 16 | 9,99±0,03 | 9,60±0,12* | 10,9±0,27* | 10,7±0,11** | 10,6±0,08** |
| 19 | 9,99±0,03 | 9,46±0,14* | 10,9±0,27* | 10,7±0,08** | 10,7±0,12** |
| 21 | 9,99±0,03 | 9,46±0,18* | 10,8±0,13** | 10,7±0,12** | 10,6±0,19* |
| 23 | 9,99±0,03 | 9,46±0,29 | 10,9±0,09*** | 10,7±0,09** | 10,6±0,12** |

Note. The difference between the arithmetic mean values is statistically significant at: * P <0.05; ** P <0.01; *** P <0.001

Table 2 - The amount of methane recovered during methanogenesis, mg / l

| Days | Control | Glauconite | Vermiculite | Perlite | Zeolite |
|------|-----------|-------------|--------------|--------------|-------------|
| 1 | 18,4±0,03 | 18,4±0,29 | 19,1±0,29 | 18,9±0,15* | 18,6±0,19 |
| 3 | 18,9±0,04 | 18,6±0,15 | 19,6±0,14** | 19,1±0,25 | 18,9±0,22 |
| 6 | 18,9±0,07 | 18,6±0,39 | 19,8±0,21* | 19,6±0,28 | 19,1±0,18 |
| 8 | 18,9±0,07 | 18,6±0,19 | 20,1±0,36* | 20,1±0,14** | 19,6±0,19* |
| 10 | 19,1±0,09 | 18,6±0,39 | 20,3±0,27* | 20,3±0,24** | 19,8±0,11** |
| 12 | 19,1±0,07 | 18,5±0,45 | 20,5±0,29** | 20,3±0,18** | 20,1±0,14** |
| 14 | 19,1±0,03 | 18,4±0,15** | 20,8±0,45* | 20,5±0,09*** | 20,3±0,18** |
| 16 | 19,1±0,06 | 18,4±0,22* | 20,8±0,52* | 20,5±0,21** | 20,3±0,16** |
| 19 | 19,1±0,05 | 18,1±0,26* | 20,8±0,51* | 20,5±0,16** | 20,4±0,23** |
| 21 | 19,1±0,05 | 18,1±0,35* | 20,7±0,24** | 20,4±0,22** | 20,3±0,36* |
| 23 | 19,1±0,05 | 18,1±0,55 | 20,8±0,18*** | 20,4±0,18** | 20,3±0,22** |

Note. The difference between the arithmetic mean values is statistically significant at: * P <0.05; ** P <0.01; *** P <0.001

The conducted researches it was established that the introduction in the manure substrate of cows of the natural minerals a vermiculite, perlite and zeolite increases the output of carbon dioxide and methane in accordance with control by 9 %, 7 and 6 %. Along with this, natural mineral a glauconite reduces in the investigated material the level of CO₂ and CH₄ by 5 %.

Consequently, experimentally proved that natural minerals a vermiculite, perlite and zeolite in anaerobic conditions increases the output of biogas from the manure of cows and can be used as stimulators of

intensification the output of biogas, while glauconite provides decrease in greenhouse gas emissions, and consequently, prevents pollution of natural environmental.

Conclusions

According to the results of the research, the most effective action on the process of methanogenesis from the investigated natural minerals at the mesophilic regime of fermentation in anaerobic conditions shows vermiculite, increasing the level of CO₂ and CH₄ by 9 %, while glauconite deactivates the process of fermentation and emission of greenhouse gases by 5 %.

Prospects for further researches are aimed search of the extended the assortment of effective means for the reduce or intensification the output of biogas at the processing of organic wastes of livestock and rational use the energy of biomass of wastes from agricultural production.

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