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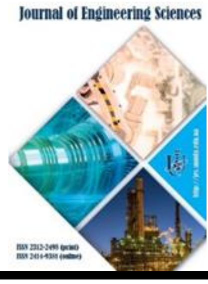

Effect of Phosphogypsum Addition on Methane Yield in Biogas and Digestate Properties During Anaerobic Digestion

Chubur V.[1], Chernysh Y.[1], Ferchau E.[2], Zaffar N.[2]

[1] Sumy State University, 2, Rymskogo-Korsakova st., 40007, Sumy, Ukraine;
[2] TU Bergakademie Freiberg, 7, Gustav-Zeuner St., 09599, Freiberg, Germany

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***Corresponding email:**
v.chubur@ecolog.sumdu.edu.ua

Abstract. The study discussed the use of phosphogypsum by-product waste in anaerobic digestion processes. Besides the production of biogas from plant substrate with the addition of phosphogypsum, the focus was placed on the enrichment of digestate with phosphogypsum as a mineral additive to increase the concentration of valuable macro-and microelements. The component composition of the obtained digestates was analyzed, and opportunities for additional research were determined. Research on the use of mineral additives in anaerobic digestion is considered promising. Phosphogypsum favors the quality of digestate as an organic mineral fertilizer with a higher content of mineral components. Furthermore, the contribution of phosphogypsum to plant substrate to achieve higher biogas production is not apparent, but with an impact on the component composition of biogas; however, there is an opportunity to consider the potential benefits of using the additive with another type of substrate waste for the anaerobic digestion process.

Keywords: biogas, anaerobic digestion, phosphogypsum, digestate, methane.

1. Introduction

Perennial grasses are considered promising energy crops due to a number of characteristics that make them particularly interesting for intensive biomass production compared to annual crops: high yield potential, high lignin and cellulose content in their biomass, high calorific value, low water content, and low complexity of field treatment. In addition, energy herbaceous crops can improve biodiversity conditions, provide opportunities for simultaneous phytoremediation and erosion control, increase soil organic carbon, and mediate water flow and nutrient content [1].

Among such perennial grasses, canary reed grass shows great energy potential in Europe for direct combustion as a feedstock for pellets and other solid biofuels [2] and biotechnology with biogas production [3].

A promising way to improve the application of beneficial elements to the soil is using digestates as a bio-fertilizer. Canary reed grass can provide an opportunity to enrich the soil with beneficial elements. This perennial herbaceous and fast-growing plant demonstrates a high biomass yield of 5-10 t dry weight/ha/year combined with a moderately high potential for accumulation of target elements [4].

It is worth noting that the application of complex compost based on mixing phosphogypsum, superphosphate, and plant residues into the recultivated soil allows reducing the content of mobile forms of heavy metals (Co, Mn, Cu, Ni, Pb) by 60-70% and more per year due to the translation of heavy metals into forms of organic complexes and metal salts that are difficult for plants to access [5]. Phosphogypsum can be considered an acid-resistant mineral carrier, which is also a source of macro-and microelements for the growth process of the necessary ecological and trophic groups of bacteria. Immobilizing carrier from phosphogypsum with an altered surface is characterized by low porosity whereby a stable biofilm can be formed on the surface of the granules. Consequently, phosphogypsum is also promising for use as an immobilizing carrier for bacteria in bioreactors.

The study aimed to evaluate the biogas production process from Phalaris arundinacea, focusing on the recovery and enrichment of digestate with phosphogypsum as a mineral additive to increase the useful macro-and microelements. Accordingly, the following tasks were set:

- to study the effect of adding phosphogypsum on the biogas yield compared with the control;
- to study the component composition of the obtained digestates and determine the prospects for further research.

2. Literature Review

The quality of digestate as a fertilizer can be changed by variations of organic waste raw material and additives in anaerobic digestion. Several studies have studied the effect of mineral additives on the biogas yield, its quality, and the component composition of the liquid and solid phase of digestates. Inorganic additives that can improve anaerobic digestion processes are considered in [6]. Inorganic mineral additives can be zeolite, magnetite, metal nanoparticles, industrial wastes, and pH-regulating additives.

Porous additives such as zeolites are well suited for ammonium removal. It has been studied [7] that the removal efficiency of ammonia nitrogen N-NH_4 increased linearly with zeolite, and in digestate effluent levels increased from 10% to 49%. The higher sorption capacity was observed in the variant of anaerobic digestion of plant waste with a smaller zeolite dose. Studies [8] have also revealed a connection between the influence of the ionic exchange of zeolites on the ability to contain the amount of nitrogen by growing strawberries. It was considered that the best efficiency of ammonium removal using zeolites is better at a pH close to 8, which matches the normal pH of the liquid digestate fraction. Nitrogen from digestate is slowly released over time and gradually converted to nitrate. There is no linear proportional effect in terms of increasing plant productivity with the addition of higher amounts of nitrogen has been observed. Therefore, the gradual release of nitrate is a good indicator.

Phosphogypsum can also become a base in complex fertilizers. It has positive results as a meliorant on saline soils to improve the physical and chemical properties and soil fertility [9].

There is known research [10] on using phosphogypsum additive in slow-release fertilizer mixtures. Such fertilizer mixtures are promising for use on acidified soils.

Moreover, using phosphogypsum in the composting process to produce organic-mineral compost with conserved nitrogen has already been investigated. The study [11] demonstrated a positive effect of mixing phosphogypsum with pig manure and cornstalk, which can effectively conserve nitrogen during composting. By adding phosphogypsum, phosphorus additives increased the NH^{4+}-N content of the compost. The higher NH^{4+}-N content might be caused by the low pH of the matrix with the addition of phosphogypsum, thus preventing the conversion of NH^{4+}-N to NH_3. Therefore, the ammonia emission is decreased.

The studies [12, 13] confirm the effects in decreasing NH_3 but increasing N_2O emissions during composting, in combination with sewage sludge or kitchen waste composting.

This means that making a mixture of slow-release fertilizers with phosphogypsum can be an excellent solution to decrease the acidity and salinity of soils. Besides blending, there is interest in exploring joint anaerobic digestion of organic waste with phosphogypsum to produce an environmentally safe organomineral fertilizer with a higher mineral element content due to the rich mineral composition of phosphogypsum (Ca, K, P, Si). Usually, the availability of phosphorus in the soil solution is relatively low, is already researched [14] the degradation of the substance in the processes of anaerobic digestion with the result of improving the availability of phosphorus for plants.

All these factors are considered promising for using organic-mineral complexes of biofertilizers. Mineral component improves both the elemental composition of the biofertilizer and acts as an additional element of nutrition in the processes of bacterial processing of organic raw materials, with an impact on the quality of the product [15].

Phosphogypsum can also become an immobilization acid-resistant carrier, providing the environment with the content of macro-and microelements for biofilm [16], which opens up the possibility of its use in technologies of anaerobic digestion.

Regarding the production of complex organomineral fertilizers, the organic part of the fertilizer is provided by the degradation of organic waste by anaerobic digestion, which has obtained two options of target products, fertilizer and biogas. Consequently, the complex production process provides obtaining green energy through biogas production during processing organic matter into fertilizer.

Furthermore, it should be mentioned that the use of phosphate waste as an additive [17] stimulated the degradation of organic waste and demonstrated the potential to reduce the risk of heavy metal pollution when applying composted organic waste to the soil by enhancing the decomposition of organic matter with transformation into humus with chelated complexes Cu and Zn. Based on composting studies, the target for continuing research on organic fertilizer (digestsate) with phosphogypsum additive for binding heavy metals in the soil was also determined.

3. Research Methodology

3.1 Characteristics of Phalaris arundinacea

Canary grass reed is characterized by a high natural concentration and variety of alkaloids and contains some anthocyanins, with lignin, cellulose, and ash content of 23%, 37%, 2% for the dry matter. Essential advantages of that plant are high yield, low cost of cultivation, and ability to grow in different conditions. Besides using bioenergy, it can be used for phytoremediation and removal of nitrogen compounds [5].

3.2 Characteristics of phosphogypsum

The phosphogypsum content (Fig. 1) includes a significant mass fraction of calcium (from 391 mg/g fresh phosphogypsum from the upper site to 236 mg/g phosphogypsum from terrace V), as well as sulfur (from 155 mg/g fresh phosphogypsum from the upper site to about 125 mg/g phosphogypsum from terraces I, II, III, and V), silicon impurities (from 8, 3 mg/g fresh phosphogypsum from the upper site to about 5 mg/g phosphogypsum from Terraces IV and V), sodium (from 6.4 mg/g phosphogypsum from Terrace II to about 3.5 mg/g phosphogypsum from Terraces III and IV) phosphorus (from about 2 mg/g fresh phosphogypsum from the upper platform and V terrace to 1.5 mg/g phosphogypsum from II terrace) and other impurities (trace elements and heavy metals) content of which is less than 1 mg/g. The content of particular elements, such as aluminum and iron, highly fluctuates in the composition of impurities.

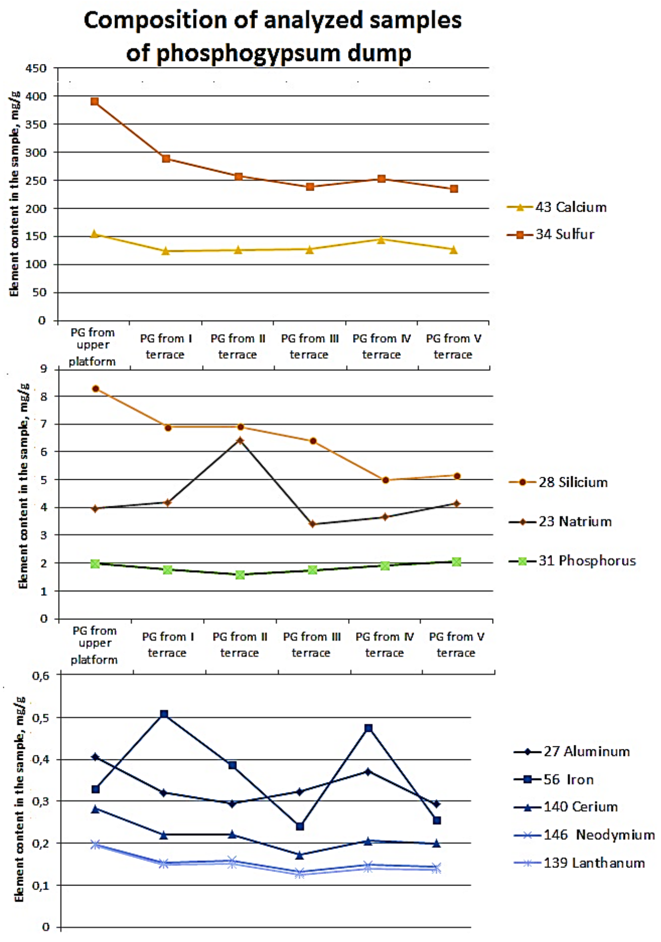

Figure 1 – Composition of elements in the analyzed samples from phosphogypsum dumps

Semihydrate gypsum transforms into dihydrate form during landfilling. In the main crystalline phase, landfill phosphogypsum includes compounds $CaSO_4$-$2H_2O$ (gypsum) and $CaPO_4(OH)$-$2H_2O$ [18].

The specificity of the physical condition of fine-milled particles of phosphogypsum, distributed in a homogeneous medium, determines phosphogypsum's relatively high mineral dispersity. Consequently, its colloids are a low rate of diffusion and unbalanced solubility, and not possible to get through the fine-pored membranes of cellular structures of organisms.

Depending on the time of phosphogypsum storage, the number of phosphorus compounds in the composition decreases, which is explained by the process of gradual transition into water-soluble forms, leaching deep into the dump or the soil of the surrounding areas. Fluorine compounds in fresh waste phosphogypsum are present for a short period in the dump. Therefore, fluorine compounds do not have time to experience the long-term effects of air-dust emission and leaching.

The increase in iron compounds, especially on terrace IV, can be explained by its washout from the upper terraces of the dump or by washout from the layers of recultivated soil located above the phosphogypsum layer.

The interaction of mineral particles of phosphogypsum with the soil substrate is based on the processes of dissolution by mineral acids, root excretions, transformation by microorganisms and effects of organic acids, and interactions of phosphogypsum particles with extracellular compounds.

Consequently, phosphogypsum waste does not contain highly toxic substances that can inhibit the functioning of microbial groups in bioprocesses.

3.3 Characteristics of the inoculum

The biogas batch experiments was conducted at the lab of TU Bergkakademie Freiberg. The inoculum for the anaerobic digestion was taken from previous tests using digestate from agricultural plant waste with 80% cow manure and 20% grass silage and residues from the farm. The component composition of the inoculum used is shown in Table 1.

Table 1 – Composition of elements in the inoculum, mg/g

K	Ca	Mg	Si	Fe	Na	P
64.1	55.6	21.1	14.6	12.6	9.9	8.2
Al	Zn	S	Mn	Cu	Ba	
1.3	1.2	0.8	0.6	0.3	0.1	

3.4 Biogas bench experiment

Canary grass plant substrate was used in a laboratory experiment to produce biogas by anaerobic digestion in a batch reactor at pH 7,0 and 39 °C. Adding 5% and 15% phosphogypsum (per dry weight of plant substrate) to anaerobic digestion on biogas production, methane yield, quality, and concentration of elements in digestate before and after the anaerobic digestion process was studied.

The conceptual diagram of the test is shown in Fig. 2.

Figure 2 – Experiments with additives of phosphogypsum: starting substrates

The anaerobic process was carried out for 20 days, and the calculation of substrate/inoculum proportions was carried out according to the VDI-RICHTLINIEN 4630 Fermentation of organic materials Characterisation of the substrate, sampling, collection of material data, fermentation tests [19]. Parameters that were determined at the beginning and the end of the digestion process were the pH and composition of load and digestate. During the whole digestion process, the biogas was analyzed with a laboratory gas analyzer to detect CH_4, O_2, and H_2S. MilliGascounters MGC-1 were used to control the biogas yield every day.

Fig. 3 shows the lab setup, which consisted of 2-liter bioreactors placed in a thermostat to maintain a constant temperature. Bioreactors were connected to the biogas collection bags via tubes, where gas counters were installed to calculate the volume of the produced biogas. The gas was collected in sampling bags and then analyzed with a gas analyzer for the composition of such gases as CH_4, O_2, H_2S.

Figure 3 – Lab stand for anaerobic digestion

The biodigestate obtained after anaerobic digestion was analyzed by inductively coupled plasma mass spectrometry (Fig. 4) to determine trace element concentrations.

Figure 4 – ICP-MS Instrument, TU Bergakademie Freiberg

4. Results and Discussion

4.1 Analysis of anaerobic digestion performance under biogas yield

Four experiments were carried out in 2 replications: inoculum, control, 5%, and 15% phosphogypsum (PG) additive. The total amount of biogas produced from 1.5 kg substrate with inoculum fluctuates from 10 to 28 liters of biogas. Details are given in Table 2. The quality of biogas varied over time. Volumetric percentages of methane content are shown in Table 3.

Table 2 – Volume of obtained biogas, ml

Day	Inoculum	5% PG additive		15% PG additive		Control	
1	200	830	680	1215	1111	1860	1317
4	329	3166	2810	4599	4839	8479	6166
7	422	7066	6411	8755	8730	16355	11888
10	634	9291	10142	11573	11242	22133	15950
13	795	10644	13235	13564	13423	25125	18123
16	902	10814	14499	15318	15657	26653	19197
19	1042	10834	15579	16276	16225	28053	20179

Table 3 – Volumetric percentages of methane content in obtained biogas, %

Day	5% PG additive		15% PG additive		Control	
3	18	16	20	17	21	22
5	47	51	47	43	52	48
7	65	67	60	58	64	61
14	60	64	60	58	61	51
19	50	69	63	58	63	50

In the batch test operating reactor, a high rate of organic load influenced the anaerobic digestion and biogas production process, which is shown in the graphs of digestion process dynamics for 18 days (Fig. 5, Fig. 6).

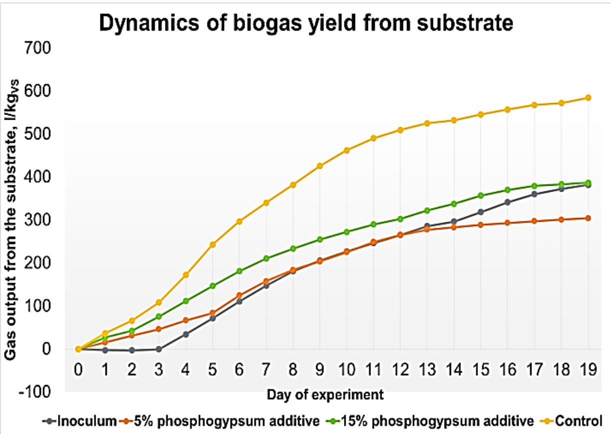

Figure 5 – Cumulative curve of biogas production from the substrate (*l/kg* $_{vs}$)

Furthermore, a considerable increase in hydrogen sulfide concentration was found both in test reactors with phosphogypsum, an increase up to 3370 ppm was registered in the experiment with 5% of phosphogypsum additive from the 5th day up to the 14th day and in the experiment with 15% of phosphogypsum additive from the 5th to the 19th day, while in the control level of hydrogen sulfide during this period varied from 50 ppm to 200 ppm.

Comparing digestion processes with mineral additive 5% and 15%, the better quality, despite close in total gas volume, has been obtained in the variant with 5% addition of phosphogypsum to the dry matter mass of plant substrate. Compared with the control, an increase in mineral load factor (phosphogypsum) leads to decreased biogas production through the predominance of sulfate-reducing microorganisms in the bacterial association. Therefore, there is a demand for additional precipitation of sulfide fraction formed in the bioreactor. From that perspective, it provides an opportunity to use this type of additive for the anaerobic digestion of raw materials contaminated with heavy metals, considering the possibility of their precipitation by excessive sulfide fraction.

Accordingly, previous studies by Chernysh et al. (2018, 2019) [20, 21] substantiated the possibility of using phosphogypsum in the anaerobic digestion of sludge from municipal sewage treatment plants to stimulate the development of sulfate-reducing bacteria and increase the yield of hydrogen sulfide in biogas, which co-precipitated heavy metals from sludge in the insoluble sulfide fraction. Since the problem of sludge utilization is still highly relevant in Ukraine, it is not used in agriculture precisely because of the presence of heavy metal compounds soluble and accumulated in the plant biomass. Therefore, an important direction is to improve the environmental quality of digestate, and its detoxification for further use. Consequently, the obtained experimental data confirm the previous results and require further study of the properties of the obtained digestate. Moreover, further research needs to select combinations of co-substrates, where the process of sulfate reducer stimulation will have an ecologically significant impact on the use of digestate as a biostimulant in agriculture and urban greening.

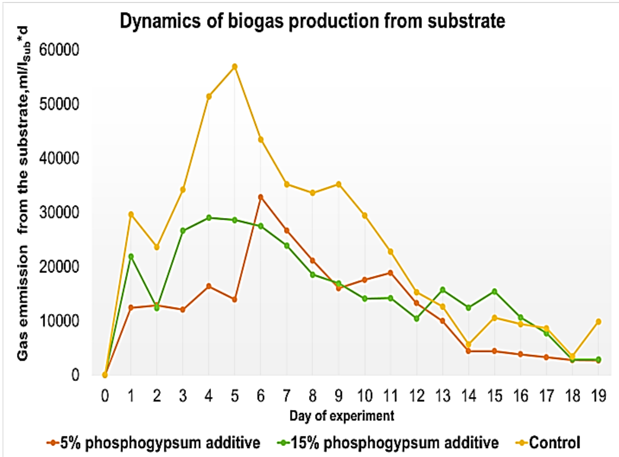

Figure 6 – Cumulative curve of daily gas production from the substrate ($ml/l_{sub} \times d$)

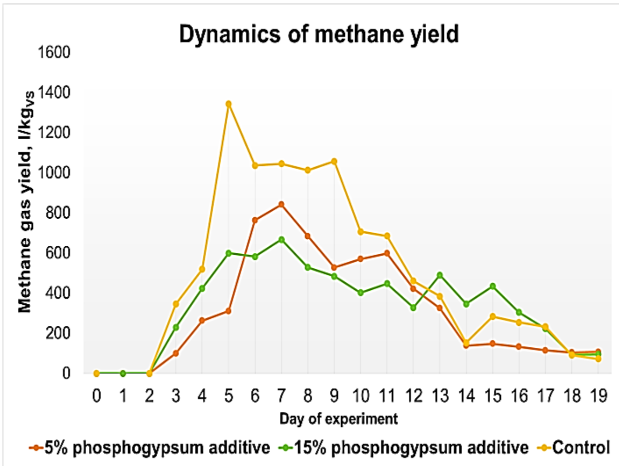

Figure 7 – Cumulative curve of methane production from the substrate (*l/kg* $_{vs}$)

There are already studied [22] the properties of some mineral additives, from municipal solid waste incineration plants and construction demolition sites, as promising sources of macro and trace elements to improve and stabilize anaerobic biogas production. The challenge in this study was to find a mineral additive that would promote anaerobic digestion without harming the microbial community of the digester. This research used additives such as incinerator slag, fly ash, boiler ash, and cement-based wastes as co-substrates for anaerobic fermentation. According to Shamurad et al. (2019), these wastes can be used as micronutrient additives to optimize the anaerobic digestion of organic materials, in particular, to prolong the efficiency of the anaerobic digestion process at a certain level of biogas productivity over a more extended time. A promising solution for dealing with substrates with high ammonia concentrations is the addition of mineral compounds (e.g., clay compounds) which can retain ionized ammonia due to their high cation-exchange capacity. In [23], the positive effect of zeolite in the anaerobic digestion process at high concentrations of ammonia was investigated. Thereby there are reasons to study the perspective of the mineral addition of phosphogypsum with livestock wastes.

4.2. Analysis of the obtained digestats

The organic part of the solid fraction of the digestate enriches the soil (improving soil conditions by reducing the humus deficit in the soil), and mineral supplement increases the soil quality [24]. The general view of the digestate of liquid and solid phases is shown in Fig. 8.

a b

Figure 8 – Image of the digestate appearance obtained after anaerobic digestion of plant substrate and phosphogypsum: a – rare phase; b – solid phase

The potassium, calcium, silicon, sulfur, and aluminum concentrations were significantly increased in the studied digestate, shown in Fig. 9. The increase in Ca, Sa, S, Al, and microdoses of the rare earth element group is related to the additional input of phosphogypsum which was rich in these components. Furthermore, the higher the level of mineral loading (percentage content of phosphogypsum), the higher the enrichment of elements in digestate, possibly due to differences in substrate availability for microorganisms and changes in chemical binding forms of elements in the composition.

Because of the high concentration of Ge (0.96 µg/g) and rare earth elements (12.26 µg/g) in the substrate used in the experiment, increasing the ratio between co-substrates leads to a decrease in the concentration of these elements (Ge 0.46 µg/g) and rare earth elements 1.6 µg/g in digestate.

Therefore, the current research aims to optimize the processes of elemental renewal, enrichment, biogas production, and identifying changes in the chemical forms of binding of target elements in digestate.

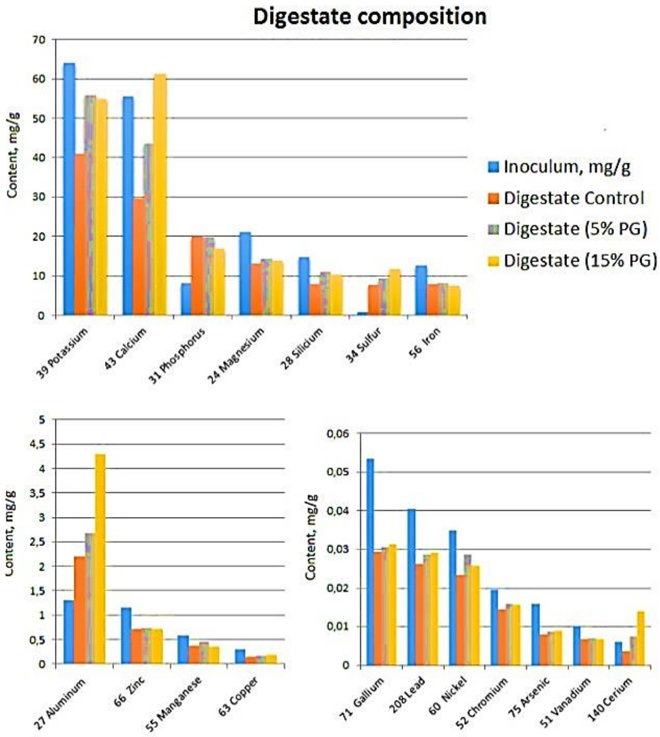

Figure 9 – Analysis of the composition of digestate obtained after anaerobic digestion of plant substrate and phosphogypsum

A decrease in phosphorus content in samples with phosphogypsum addition was noted compared to the control sample (from 19.8 µg/g to 15.1 µg/g). Hence, in the liquid fraction were isolated compounds of phosphorus, which can be used in complex with the obtained organomineral product.

Currently, an important goal is to reduce the risk of heavy metal contamination after returning biogas to the field as fertilizer. Thus, a study by Li Yi et al. (2016) [25], which was focused on reducing heavy metal pollution in pig manure, used anaerobic fermentation technology to study the effects of adding exogenous zeolite on biogas production, methane content, and changes in the proportion and chemical fractions of heavy metal zinc in digestate. The results show that zeolite does not significantly affect gas production and methane content during biogas fermentation. After fermentation within the zeolite addition, 89.88% of Zn heavy metal is contained in the biogas sludge, only 10.12% in the biogas slurry. Zeolite may be a passivator of metals in the anaerobic fermentation process.

Therefore, the relevant topic still remains the search for effective local bacterial biosorbents that can survive even under toxic environmental conditions in various metabolic states.

5. Conclusions

The use of mineral additives in anaerobic digestion is a viable factor for further research, particularly the phosphogypsum additive. However, phosphogypsum's positive influence on the improvement of digestate quality can be used as an organic mineral fertilizer with enriched mineral components. It is also definite that mixing phosphogypsum additive with plant waste does not produce a positive effect on biogas formation; nevertheless, it is possible to analyze the prospects of using the additive with animal waste with increased content of nitrogen compounds.

Subsequent studies will focus on studying organic-mineral digestion products with the addition of phosphogypsum after the digestion of various co-substrates based on organic waste under micro-field conditions.

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