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ORIGINAL ARTICLE

Co-digestion of poultry litter with cellulose-containing substrates collected in the urban ecosystem

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Abstract
This study examined the influence of fallen leaves from the urban ecosystem as a cellulose-containing additive in the process of anaerobic digestion of poultry litter. Using X-ray fluorescence analysis, the elemental composition of the mineral component of dried leaf samples was determined. In the process of studying the anaerobic digestion of poultry litter with cellulose-containing co-substrate, the doses of the dry leaves were analyzed at 15%, 30% and 45% of the dry matter (DM) of leaf additives as a co-substrate. The obtained results indicated that the cellulose-containing co-substrate from the dried leaves after preliminary preparation can intensify biogas evolution and reduce the lag phase of the production of methane in the anaerobic digestion of poultry litter. Additionally, the optimal content of dry leaves was determined at 30% on the DM. A further increase in the percentage did not lead to significant changes in the indicators of anaerobic digestion. The use of a modified Gompertz model and the kinetic parameters of the methanogenesis process with the formation of a system of differential levels will provide more insights for their effective use in predicting and optimizing anaerobic digestion, which will be carried out in further studies.

Keywords Anaerobic digestion · Poultry litter · Fallen leaves · Co-digestion · Cellulose-containing co-substrate · Biogas

1 Introduction

In Ukraine, anaerobic digestion technology is still fairly new and has only recently been introduced to the market [1]. As of 2018, there were more than 50 biogas-producing facilities in Ukraine, 33 of which were working on organic waste. As of 1 April 2018, the total capacity of biogas plants was 44 MW [2]. In 2019, Ukraine took eighth place in the rating of investment attractiveness of the "green" energy of developing countries (Government portal https://www.kmu.gov.ua). The use of biogas in decentralized energy supply also helps to reduce energy imports and improve the security of energy supply, particularly in rural areas. In Ukraine, the state authorities only support the production of electricity from biogas [3]. In 2019, the green energy sector produced about 3.7% of the total electricity, but it costs 8% of the total electricity in the country. For example, Havrysh et al. [4] stated that in the range of 75–1300 kW the average cost of electricity is 0.1649 Euro/kWh. Anaerobic digestion technology is still among the most expensive renewable energy sources. Thus, the green tariff has become a financial burden on the state budget. To reduce it, lawmakers took the initiative to replace the tariff with auctions. They expect green auctions to guarantee a reasonable price for renewable energy.

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As for biomethane, its production and disposal are not regulated by law [4].

Overall, the potential for the implementation of anaerobic digestion technology for waste processing in Ukraine is significant. According to Pavliukh et al. [5], the processing of 120 million tons of organic waste in dry form can produce 36–75 billion m^3 of biogas in Ukraine. Furthermore, the development of the bioenergy potential of Ukraine is possible with the integrated use of various types of organic waste with the production of both biofuel and high-quality fertilizer (digestate).

At many poultry farms, the amount of litter, generated during the year, reaches tens or even hundreds of thousands of tons (Programme to Support the Green Modernization of the Ukrainian Economy, 2016). The disposal of poultry litter has become a difficult problem for many poultry farms, as it requires large amounts of material, technical and monetary resources, as well as large areas of agricultural land. Fresh litter is a source of unpleasant smells, poisonous gas emissions (ammonia, hydrogen sulfide), it can contain a significant amount of weed seeds and helminth eggs and it is also a favourable environment for the development of pathogenic microorganisms. In the case of untimely processing, such litter becomes a source of environmental pollution (atmosphere, water bodies, soil, groundwater) [6]. It is also not recommended to use fresh manure as a fertilizer if it is not processed in an appropriate way, as described in the "Programme to Support the Green Modernization of the Ukrainian Economy under National Waste Management Strategy for Ukraine" (Consortium Resources and Waste Advisory Group Limited, 2016).

Also, the problem of how to utilize the fallen leaves and plant residues in agriculture is relevant for many areas — both urban and rural ecosystems [7]. Burning plant residues leads to the destruction of the soil cover and death of hibernating beneficial insects. Fire destroys the roots of herbaceous plants and seeds, damages the lower parts of trees and can also cause uncontrolled fires which pose a threat to public health and the environment. On the other hand, the systematic introduction of digestate into the soil ensures the development of useful ecological-trophic groups of microorganisms and the optimization of microbial processes in the soil during humus formation. This allows the maintenance and improves the productivity of the land and, as a result, reduces the cost and improves the quality of agricultural products.

The urgency of solving the problem of the utilization of poultry waste final effluents has led to a sharp decline in crop quality, dangerous pollution of groundwater, surface water, air basin and increasing animal morbidity (Gritsun et.al. 2012).

The digestion of bird manure with biogas and fertilizer is being investigated in many countries and requires further optimization and combination with other organic substrates, in particular with those containing cellulose [8]. At the same time, for Ukraine, chicken droppings are a rather promising organic substrate due to the developed poultry production industry.

However, biogas obtained from the anaerobic digestion of poultry litter usually contains low levels of carbon and nitrogen and cannot be used at an industrial scale. Past works (such as [9–11]) have shown that the potential of the litter can be increased by combining it with other feedstocks with high methane potential content, such as plant residues.

Nie et al. [12] studied the factors of influence on the process of stabilization of chicken manure mono-digestion, which was achieved in the recirculation of ammonia depleted liquid digestion fraction and high feed rates from 5.3 to 6.0 gVS/(L*d) and at free ammonia nitrogen to 0.86 g/l. But at the same time, the process faced inhibition, which requires further optimization. When compared to the work of Böjti et al. [13] where treated chicken manure (T-CM) was used, which led to water extraction and an increase in the C/N ratio in chicken manure from 7.45 to 19.81. The combination of T-CM with corn silage further increased methane production, presumably by improving the C/N concentration [13]. Corn silage has a good practice in anaerobic digestion processes. However, corn silage is not just a part of a cow's diet, but a complete multi-component feed that has a huge potential to influence profitability. It is convenient, cheap and easy to prepare. Corn silage is rich in starch and fibre energy. It is corresponding to the case of Ukraine, as it is very demanded in animal industries [14].

The main types of crop waste are straw, chips, cereals and cereal husks, stems and leaves of agricultural plants, corn cobs and kernels, flax fibres and other vegetable raw materials. The possibility of using organic waste (corn, straw, branches, fallen leaves, potato peelings) for biogas production was experimentally confirmed. The influence of the initial fraction size and the temperature on the biogas yield has been studied (Pavliukh et.al. 2019).

Due to the high natural moisture content of corn production waste for grain (up to 60%) as a promising direction for their utilization for energy purposes, Geletukha et al. (2014) proposed ensiling with subsequent biogas production [15].

Vegetable waste as a cellulose-containing additive can have some negative properties, which requires a very careful approach to their use. Thus, straws may contain chlorine and alkali metals, which may adversely affect the process of anaerobic digestion. As for Ukraine, it is quite possible to assume that the content of chlorine and alkali metals in straws is less than in the straw of other countries. This is due to a significant reduction in the application of mineral fertilizers to crops over the past 20 years [15]. According to the research by Geletukha and Zheliezna [15], the chlorine content is 0.2% by weight of dry matter (DM), which is close to the indicator of raw straw.

Biogas production from straw, leaves and algae was investigated by Dubrovskis et al. [16]. The average specific methane yield from fallen leaves of trees was 204 ± 19 l·kgVSA-1 per unit of volatile solids added (VSA), and the average methane (CH_4) content was 54% [16]. The co-digestion of fallen leaves and sewage sludge was investigated by Yang et al. [17] for biohydrogen production. The biohydrogen yield reached 37.8 mL/g-volatile solid (VS) added at the mixing ratio of 20:80, which was higher compared to the mono-digestion of sludge (10.3 mL/g-VSA) or the leaves (30.5 mL/g-VSA) [17].

In the research by Liang and Zhang [18], wheat straw and fallen leaves were used as raw materials for solid-state anaerobic digestion (AD). Straw, leaves and a mixture of them were aerobically pretreated respectively. The comparison of the experiment results showed that the volatile solids (VS) gas production of the straw is higher than that of the fallen leaves. The fermentative materials of leaves have the most accumulation and the longest retention time of gas production [18].

Anaerobic digestion of fallen leaves provides the utilization of this type of plant waste and biogas production of up to 350 dm^3 from 1 kg of dry matter [19].

The problem of disposal of fallen leaves can be solved by the biological destruction of leaves in anaerobic conditions together with bird droppings. But it is important to determine the ecological characteristics of fallen leaves for their most effective use in the process of anaerobic digestion as stimulating and environmentally friendly additives. This is especially important for plant wastes that are generated in the city, as they are characterized by a higher content of toxic substances than those that are generated on the periphery.

Therefore, this work aims at studying the fallen leaves of the urban ecosystem (of Sumy, Ukraine) as a cellulose-containing additive in the process of anaerobic digestion of poultry litter.

To achieve this, the following tasks were set:

- analysis of the volume of production of poultry litter, as well as the prospects for using chicken manure for bioenergy purposes;

- study of the mineral composition of leaves of *Acer platanoides L.* from different territorial locations of the urban ecosystem of Sumy, Ukraine;

- study of the dosage effect of cellulose-containing additives on the process of anaerobic digestion of chicken manure.

2 Materials and methods

2.1 Characteristics of the studied substrate

The results of measurement of dry matter, organic matter, ash etc. of the tested chicken manure are given in Table 1.

The pH of the substrate was also measured, which was 7.55. The moisture rate was 51%.

In the samples of fallen leaves (*Acer platanoides L.*), the content of lignin is within 10–13% DM and cellulose 19–21% DM.

2.2 Experimental setup

The intensity of the digestion was studied by the amount of biogas formation from samples of chicken manure: (i) without co-substrate; (ii) with the co-substrate of fallen leaves. The experiment was conducted simultaneously with periodic cultivation. Raw sewage sludge used in this work was collected from waste water treatment plant (WWTP) corresponding to a population of approximately 290,000 inhabitants located in the city of Sumy, Ukraine. Dispersion of a mixture of chicken manure, phosphorus-containing components and fallen leaves was performed at a rotational speed of the rotor of the dispersant 12 s^{-1} for 1 min. The pre-dried leaves were crushed and sprinkled with hot water (308 K).

The anaerobic digestion process was carried out in a glass cylinder (bioreactor with a capacity of 1 dm^3, tightly closed with a rubber stopper). Hermetically sealed glass containers for collecting biogas and a measuring container for measuring volumes of biogas displaced water were connected to the bioreactor, mixing the fermented mass by setting it on a magnetic stirrer (2 s^{-1}).

Maintaining a constant temperature of the mesophilic mode of anaerobic digestion was performed by a heater with a dry air thermostat TC-20 ("Mediko Instrument Plant — Medaparat" Ltd., Ukraine) immersed in a bioreactor. To minimize heat loss from the bioreactor, a foam insulation was used all around the bioreactor. The foam thickness was 20 mm.

Figure 1 shows a diagram of a laboratory installation of anaerobic digestion of organic waste.

The cylindrical tank/bioreactor (1) with a volume of 1 dm^3 was loaded with the test mixture, sealed with a stopper (3). A tube was connecting with the bioreactor (1) and the gas receivers (8). The gas receivers (8) were filled with water. The heater with a thermostat (2) was installed in the cylinder (1), placed on a magnetic stirrer (5) and covered with a foam cap (4). The cylinder and all connections were then checked for leaks. When the set temperature was reached in the bioreactor (1), volume measurements were performed.

The tests were performed at the same time. The daily volume of biogas produced was monitored every day in a measuring cylinder with water. The study of the biogas composition was conducted on a gas chromatograph Selmihrom-1 (PAT "Selmi", Ukraine).

The primary pH of the chicken manure was 6.5, and after the addition of the cellulose-containing additive (dry leaves), the pH increased to 7.0–7.3. At the end of the experiments, the pH was close to 8.0.

Table 1 Characteristic of chicken manure

Dry matter, %	Total nitrogen (N), %	Mass fraction of organic matter in terms of carbon (C), %	Mass fraction of total phosphorus (P), %	Ash content, %	The standard deviation of data	C:N ratio
48.9	5.8	15.9	2.3	42.1	±0.2	2.74

Pretreatment of the substrate included a separate hydrolysis stage. Dry leaves were mixed with poultry manure and brought to a moisture content of 90% with water (308K). The substrate was incubated for 10 days with constant stirring in a closed container.

The anaerobic digestion was performed in mesophilic temperature mode (308 K).

The species of *Acer platanoides L.* was chosen as it is salt-tolerant and was distributed in all sampling locations. Also, it is included in the list of tree species that are recommended for use in landscaping city streets and roads in Ukraine under Order 27.11.2017 no 310, on approval of the Model Regulations for the Improvement of the Territory of a Settlement, published by the Ministry of Regional Development, Construction, and Housing and Communal Services of Ukraine.

Typical samples of fallen leaves were used by composition; fractions were used to assess the content of heavy metal compounds. Two types of green areas were selected: a park area and green areas near the city's highways.

The research used standardized measurement methods [20]. Averaging at sampling sites was performed by the method of quartering for a square area of 100 m^2. Selected fallen leaves were stored in an air-dry state in polyethylene containers type MN-5. The selection was in the following locations:

- the ecosystem of Kozhedub Park in Sumy (Ukraine);
- the ecosystem of Kharkivska Str., Sumy (Ukraine).

2.3 Research methods

The pH of substrates was monitored at daily intervals using a pH meter ionomer pH-150MP (Gomel Measuring Instruments Plant, Belarus) with a glass combined electrode "EX-10603", with the limit of the main error being ± 0.05 pH units.

The humidity of the samples was determined by the conventional method of the gravimetric method, DSTU ISO 114652001, with the drying of the sample at 378 K. At the same time scales laboratory equal shoulders of the VLR-1 model of the 3rd class with a permissible error of 10 mg, drying cabinet ShS-40, desiccator, boxes were used.

The elemental analysis of the composition of the samples was performed on an X-ray fluorescence analyzer Elvax (Elvatech Ltd., Ukraine). Limits of detection of impurities of heavy metals were not less than 10 ppm. All measurements were performed and dried at n.u. and ground into powder samples in cuvettes with a volume of 30 cm^3.

A study of the biogas was carried out on a laboratory gas chromatograph SelmiChrom-1 (Ukraine). The content of biogas components was measured on the final day of the experiments.

2.4 Modelling anaerobic digestion and verifying mathematical models

From the practice of modelling anaerobic digestion, the following types of models were often used: the Gompertz model

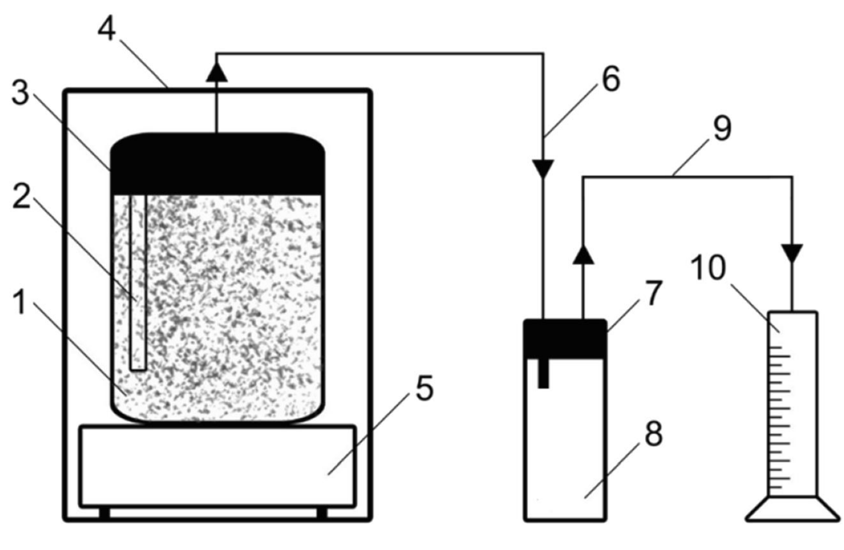

Fig. 1 Schematic of the laboratory installation: 1 — bioreactor; 2 — heater with thermostat; 3, 7 — airtight cover; 4 — hermetic heat-insulating cap; 5 — magnetic stirrer; 6, 9 — tube; 8 — a glass for collecting biogas; 10 — measuring cylinder

in various modifications [21–23] and regression models [24–26].

In this paper, we decided to compare these models as applied to the process of co-digestion of poultry manure with the addition of leaf from the park's ecosystem. At the same time, Pearson's correlation coefficients (r) were used as the criteria for evaluating mathematical models.

3 Results and discussion

3.1 The environmental issue of poultry litter in Ukraine and its bioenergy potential

Table 2 shows the changes in the number of different bird species in Ukraine according to the State Statistics Service of Ukraine [27], which shows the "growing tendency" of the number of poultry farms and, respectively, the products of birdlife activities such as litter.

A litter generation in the range of years 2015–2020 were made (Table 3). For the analysis of the current situation with poultry litter, the calculation method described by Bryukhanov et al. [28] was used. The bioenergetic potential of this waste is an important source of renewable clean energy from anaerobic digestion.

Ukraine has an animal population of 2.5 million cattle, 7.9 million pigs and 230.3 million poultry. In terms of waste, it means up to 15 million m^3 of cattle manure, 166 million m^3 of pig manure and 1725 million m^3 of poultry litter per year. From this waste, it is possible to get from 2831 million Nm^3 to 4711 million Nm^3 of biogas per year, or from 1779 million Nm^3 to 2862 million Nm^3 of biomethane per year [29].

As seen in Table 3, the annual output of chicken manure production is 92% of the total amount of generated poultry waste in Ukraine. This indicates a significant raw material resource that can be used for bioenergy purposes.

However, the estimates of waste yield are only approximate. The estimates of manure, litter and biogas yields are highly site specific and technology specific. In particular, the generation of chicken manure depends on the age of the animal, as well as the conditions of the housing. For example, depending on the conditions, manure can have a high water content, which is one of the decisive factors in digestion, because a high water content reduces the biogas intensity from a unit volume in the digester [29]. Often, the organic dry matter content is much lower than the values presented. Other reasons can be different feed quantity and quality, which therefore strongly influence the final composition [29].

One of the biggest environmental problems of industrial farms is the formation of large amounts of manure or litter. Ukraine does not yet have strict requirements on how farms should dispose of waste. The manure may accumulate and be stored in special storage facilities (with possible subsequent composting or vermiculturization of the fraction during its separation into fractions) and undergo anaerobic biological treatment for biogas production, physical-chemical or mechanical-biological treatment [3].

However, in practice, most farms use the option of waste accumulation and storage — litter being accumulated and stored for some time in lagoons [4]. Afterwards, the manure is applied to the fields as organic fertilizer. Such waste management does not provide the necessary solution for an environmental problem if the farm is small or medium scale and the waste generation is, therefore, in adequate quantities and if the safety rules for waste management and the application of waste to the soil are observed [29]. Under these conditions, litter is a valuable organic fertilizer. Problems arise when waste management regulations are broken and when this method is applied on large-scale industrial farms. Industrial farms have hundreds of thousands of animal heads or millions of poultry heads per year. Thousands of cubic meters of waste is produced, is collected in lagoons and is stored for months up to a year before being taken to fields.

In Ukraine, about 50% of cattle breeding farms are industrial [4, 29, 30].

In most countries with developed poultry farming, poultry enterprises have very strict requirements regarding the methods of storing and processing manure. The main ones are as follows [31]:

- Exclusion of the possibility of the product itself and liquid effluents getting into groundwater and open water bodies;

- Minimization of ammonia emissions into the atmosphere;

Table 2 The number of poultry in farms of all categories

Bird species	Year					
	2015	2016	2017	2018	2019	2020
	Number of poultry per year					
Chickens	193,885,500	186,354,300	184,335,900	186,737,200	191,967,900	200,251,0700
Gooses	5,365,400	5,114,700	4,183,400	4,116,900	4,159,700	4,015,800
Ducks	11,310,400	10,150,200	10,876,400	10,953,700	11,680,000	11,418,300
Turkeys	2,114,700	1,825,000	1,575,300	1,951,000	1,706,900	1,939,000

Table 3 The annual output of poultry litter (aggregated calculation)

Bird species	Year						The average value, tons
	2015 Tons per year	2016	2017	2018	2019	2020	
Chickens	7,755,420	7,454,172	7,373,436	7,469,488	7,678,716	8,100,428	7,638,610
Gooses	214,616	204,588	167,336	164,676	166,388	160,632	179,706
Ducks	452,416	406,008	435,056	438,148	467,200	456,732	442,593
Turkeys	84,588	73,000	63,012	78,040	68,276	77,560	74,079

- Exclusion of the spread of unpleasant odours on the territory of settlements travel roads and other public facilities;

- Neutralization of pathogenic microorganisms, helminth eggs, weed seeds;

- Exclusion of salts of heavy metals, radionuclides, pesticides and other toxic substances from entering the soil, underground waters and surface water bodies together with droppings or products of its processing;

- The presence of sufficient areas of farmland for the use of manure in permissible quantities as fertilizer.

Some of the above-mentioned requirements, such as the control of ammonia emissions into the atmosphere or the availability of sufficient agricultural land, which are very important for environmental protection, unfortunately, do not have legal force in Ukraine. As a result, some poultry enterprises are created that do not have the appropriate area for the use of manure, a sanitary protection zone or the corresponding agreements with other agricultural enterprises.

Thus, manure and litter are being a source of ammonia, methane and other gases in the air. When stored in open lagoons or when applied to fields in large quantities, the local population living close to industrial farms suffers from an unpleasant odour [29]. In Ukraine, such odour components as methylmercaptan, dimethylamine and dimethylsulfide are not regulated. Only the basic connections, such as methane, ammonia and nitrogen dioxide, are normalised, but also modern borders of sanitary-protective zones are usually insufficient to prevent the exposure of the local population to a smell that causes a decrease in well-being, immunity, allergic reactions and/or respiratory diseases.

Poultry litter, especially chicken manure, are valuable organic fertilizers with a high content of nutrients (nitrogen, phosphorus, potassium and trace elements) [32]. At the same time, prolonged storage of manure in open areas causes irreparable damage to the biosphere: the atmosphere is polluted by gases resulting from microbiological processes, hydrosphere — by components of manure dissolved in rainwater. As studied by Charles [33], poultry manure and bedding may also contain harmful pathogens as well as chemical residues in the form of veterinary medicines (antibiotics, coccidiostats, etc.). Everything depends on the diet, management practices and regulation of poultry farms in a given region. Chicken manure storage near poultry farms pollutes the territory and groundwater, and the application of excessively high doses (more than 300 m^3/ha) in the soil causes a sharp increase in nitrate content in agricultural products [34]. One of the main reasons for the environmental hazard of manure is the low quality of technological operations to remove it from the premises, as well as improper storage, transportation and the most important use as an organic component in the production of fertilizers. As stated in the study of Bezubtsev and Shmid (2013) in case of non-compliance with the conditions of manure storage on the ground floor, the content of mineral nitrogen in the surface soil layer (0.4 m) can reach 4950 kg/ha, including up to 2500 kg/ha of nitrate form of this element, which is 17 times higher than in uncontaminated soil. Unsatisfactory storage and excessive use of manure not only causes significant harm to the environment but also leads to the loss of a large amount of valuable organic fertilizer needed for agricultural land. A solution to the problem of utilization of manure of anthropogenic origin ensures the improvement of the ecological environment and soil fertility.

3.2 Prediction of poultry litter production

To predict the volume of poultry litter production, the polynomial trend was calculated for the analyzed data and future periods using the trend equation:

$$y = 85.262x2 - 525.55x + 8184.9 \ (R2 = 0.9968). \quad (1)$$

The time series of chicken manure formation is formed by years with two variables: year (x), the volume of chicken litter in thousand tons per year (y).

When building the forecasts, a time scale with equal intervals between data points was selected — 1 year. The annual intervals are selected according to the statistical data state on the first day of each year. The year 2021 was selected as the initial year from which the forecast was made. In this case, to build a forecast for 2021–2025, data for 6 years preceding

2021 were used; this allowed to build a "retrospective forecast".

The confidence interval was selected as 95%, which allowed the establishment of a range around each predicted value, which according to the forecast (with normal distribution) 95% of the points related to the forecast for the next 5 years were expected to be obtained.

Taking into account the size of the confidence interval, the lower and upper limits were chosen and accepted as possible forecast scenarios. At the same time, the lower boundary of the confidence interval was used as a negative projection — a decrease in the rate of chicken dung formation. Likewise, the upper boundary of the confidence interval is accepted as a positive forecast — an increase in the rate of chicken droppings formation.

The obtained forecasts of chicken manure production are constructed with a probability of 95% and are presented in Fig. 2. Poultry meat and eggs are essential products in human nutrition. Therefore, these products are in considerable demand both in the domestic market and abroad. The processes of transformation of the state that took place in Ukraine in the post-Soviet period had a significant impact on the development of poultry farming. The decrease in sales is associated with a decrease in the purchasing power of the population, which leads to a decrease in production. According to the analysis of statistical reporting data of enterprises, the development of poultry farming in the period from 1990 to the present day can be divided into two stages — the decline in poultry production from 1990 to 1997 and the revival of production from 1998 to the present day [35].

However, it is established in the poultry market [36] that during 2016–2018 the total projected demand for poultry eggs in Ukraine decreases from 16,990 million eggs in 2015 (by domestic production — 16,920 million eggs) to 14,260 million eggs in 2018 (by domestic production — 14,220 million eggs) or by 2.73 billion eggs (by 16.1%) of the probable decline in purchasing power in Ukrainian.

As seen from Fig. 2, the forecast is positive, and in the future, the litter yield will increase, as evidenced by the growth in the productivity of poultry farms and the actualization of this business in Ukraine (Consortium Resources and Waste Advisory Group Limited, 2016). The analyses of changes in the animal population and production volumes suggest that the general trend is characterized by an increase in indicators [37], which confirms the forecast. Among the reasons for the increase in volumes, it is possible to define: increase of economic efficiency of activity of the enterprises of poultry farming branch at the expense of modernization of manufacture, creation of new links of vertically integrated structures and introduction of control systems of quality of production. The results of the study showed that the current state and potential of the poultry industry have prospects for development.

Therefore, the issue of chicken manure utilization is becoming more and more relevant for Ukraine, and biogas technology can be an energy-efficient and environmentally friendly solution.

3.3 Study of the mineral composition of leaves of trees of the genus *Acer platanoides L.* from different territorial locations of the urban ecosystem of the city of Sumy

The leaves of *Acer platanoides* contain a significant amount of biopolymers, including carbohydrates (fibre, starch) and other biologically active substances that can serve as a nutrient medium. In urban ecosystems, fallen leaves in addition to useful nutrients may also contain toxic compounds including heavy metals.

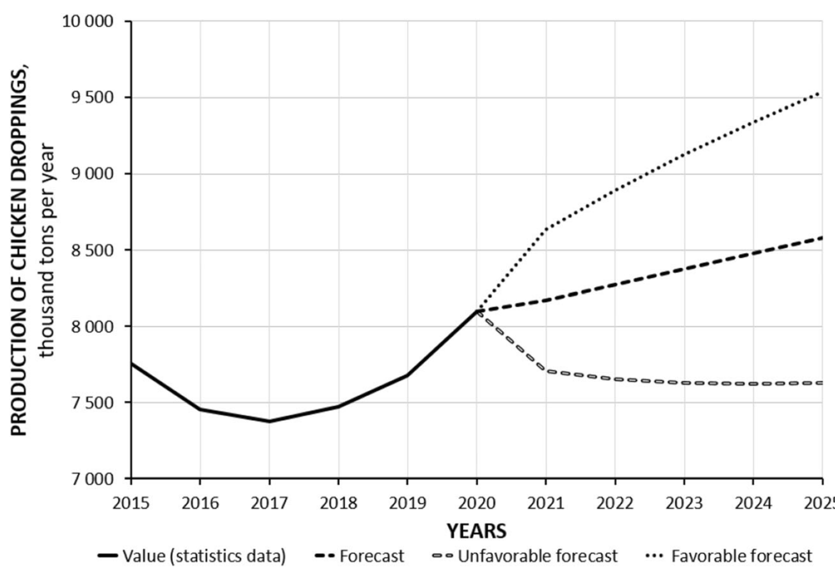

Fig. 2 Forecast of the dynamics of the formation of chicken manure in Ukraine

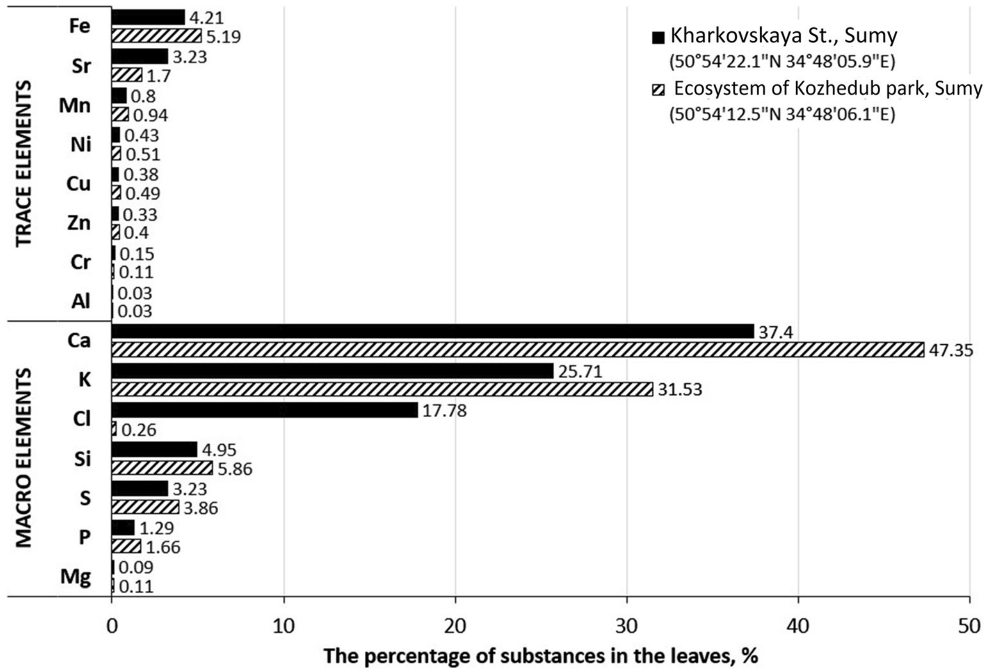

Fig. 3 Comparative diagram of the mineral composition of *Acer platanoides L.* leaves from different locations, Sumy (Ukraine)

Using X-ray fluorescence analysis, the elemental composition of the mineral component of leaf samples was determined. Accordingly, a diagram (Fig. 3) was built of the percentage distribution of elements in the composition of leaf samples from the locations of the urban ecosystem of different technogenic load.

Technogenic load is the level of impact of human activity on the environment, conditionally subdivided into permissible (with compliance with MPC) and environmentally hazardous. In this case, the technogenic load is characterized by the influence of emissions from transport and enterprises.

As shown in Fig. 3, leaf samples from the location on Kharkivska str. with heavy traffic has differences in the spectrum of the mineral element in comparison with samples from the green park zone with a low level of anthropogenic impact. In particular, it refers to the presence of a high peak in chlorine.

As we can see from the diagrams of the mineral component (Fig. 3), the leaf samples contain a significant percentage in the mineral composition of Ca and K, which are biogenic elements and useful for the development of microorganisms. It should be noted that fallen leaves contain a significant amount of biopolymers, including carbohydrates (fibre, easily fermentable carbohydrates, starch, etc.) and other biologically active substances that can serve as a nutrient medium.

Thus, in the samples taken from Kharkivska str., in areas with high levels of anthropogenic impact (emissions of gaseous substances from vehicles and enterprises), there is a significant content of Cl, which indicates the accumulation of chlorine salts in the leaves, which can be toxic to the digestion process [38]. It should also be noted that such ions as Ca^{2+} and Mg^{2+} can counteract ammonia inhibition of anaerobic digestion. It is a phenomenon that occurs when the toxicity of one ion decreases in the presence of other ions [39]. This is an important aspect as chicken manure has a higher nitrogen content than other farm animal waste [40].

3.4 The effect of the dose of cellulose-containing additives on the process of anaerobic digestion

To avoid the inhibition of ammonium nitrogen, substrate (poultry litter) dilution with water, co-digestion with other wastes, methanogenic consortium adaptation, ammonium nitrogen fixation and deposition in the form of struvite, ion exchange materials, anammox and denitrification are used [41].

The possibility of co-digestion with cellulose-containing additives is one of the most effective ways to improve the qualitative and quantitative indicators of anaerobic digestion of chicken manure.

In the process of the present research on chicken manure anaerobic digestion with cellulose-containing co-substrate (dried leaves after preliminary preparation), the doses of additives were analyzed: 15%, 30% and 45% according to DM; zero tests (anaerobic digestion without co-substrate) were also performed (Fig. 5).

The highest yield in the first week of the study was observed in the digestion of chicken manure with 30% on DM of the co-substrate content; at 15%, the biogas yield did not increase. When the content of the additive increased to 45%, the biogas yield did not increase. On day 16, the intensity of biogas formation in the sample from 30% and 45% of the additive decreased to the samples with the content of the additive 15% on DM, indicating a gradual decrease in the metabolic activity of methanogenic microorganisms due to reduced nutrient content in the fermented mixture.

Using the Excel spreadsheet, the dependence of the biogas volume on the retention time at different doses of cellulose-containing co-substrate was simulated (Fig. 4):

- For 45% on DM of leaf additives as a co-substrate (r = 0.9764)

$$y = 5427.59 \cdot 0.0054^{0.60^{(x-1)}} \quad (2)$$

- For 30% on DM of leaf additives as a co-substrate (r = 0.9751)

$$y = 5882.66 \cdot 0.0054^{0.63^{(x-1)}} \quad (3)$$

- For 15% on DM of leaf additives as a co-substrate (r = 0.9626)

$$y = 4321.59 \cdot 0.0093^{0.63^{(x-1)}} \quad (4)$$

- without the cellulose-containing co-substrate (r = 0.9233)

$$y = 4152.11 \cdot 0.0013^{0.76^{(x-1)}} \quad (5)$$

Using the Excel spread sheet, experimental data were processed to obtain regression equations for the dependence of the volume of biogas on the retention time at different doses of cellulose-containing co-substrate (Fig. 5):

- for 45% on the DM of leaf additives as a co-substrate (r = 0.9941)

$$y = 0.0002x^6 - 0.0295x^5 + 1.4875x^4 - 32.998x^3 + 305.65x^2 - 466.88x \quad (6)$$

- for 30% on DM of leaf additives as a co-substrate (r = 0.9923)

$$y = -0.0001x^6 - 0.0056x^5 + 0.8075x^4 - 24.832x^3 + 271.81x^2 - 445.71x \quad (7)$$

- for 15% on DM of leaf additives as a co-substrate (r = 0.9854)

$$y = -0.0003x^6 + 0.0122x^5 + 0.0135x^4 - 8.5042x^3 + 123.9x^2 - 118.23x \quad (8)$$

- without the cellulose-containing co-substrate (r = 0.9825)

$$y = -0.3726x^5 + 9.7467x^4 - 79.138x^3 + 232.61x^2 - 159.49x + 20.892 \quad (9)$$

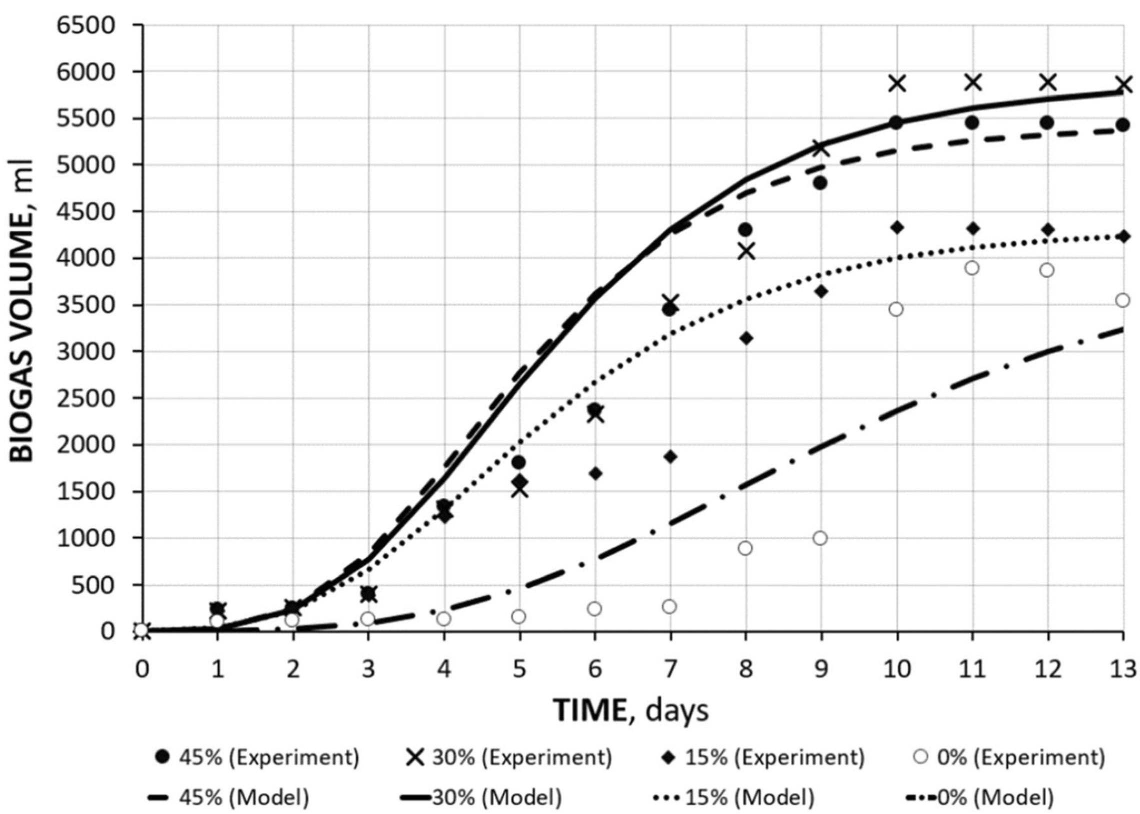

Fig. 4 Experimental rates of biogas yield in the co-digestion of poultry litter with varying amounts of cellulose-containing substrates and comparison to analytical data fitting simulations based on the Gompertz equation

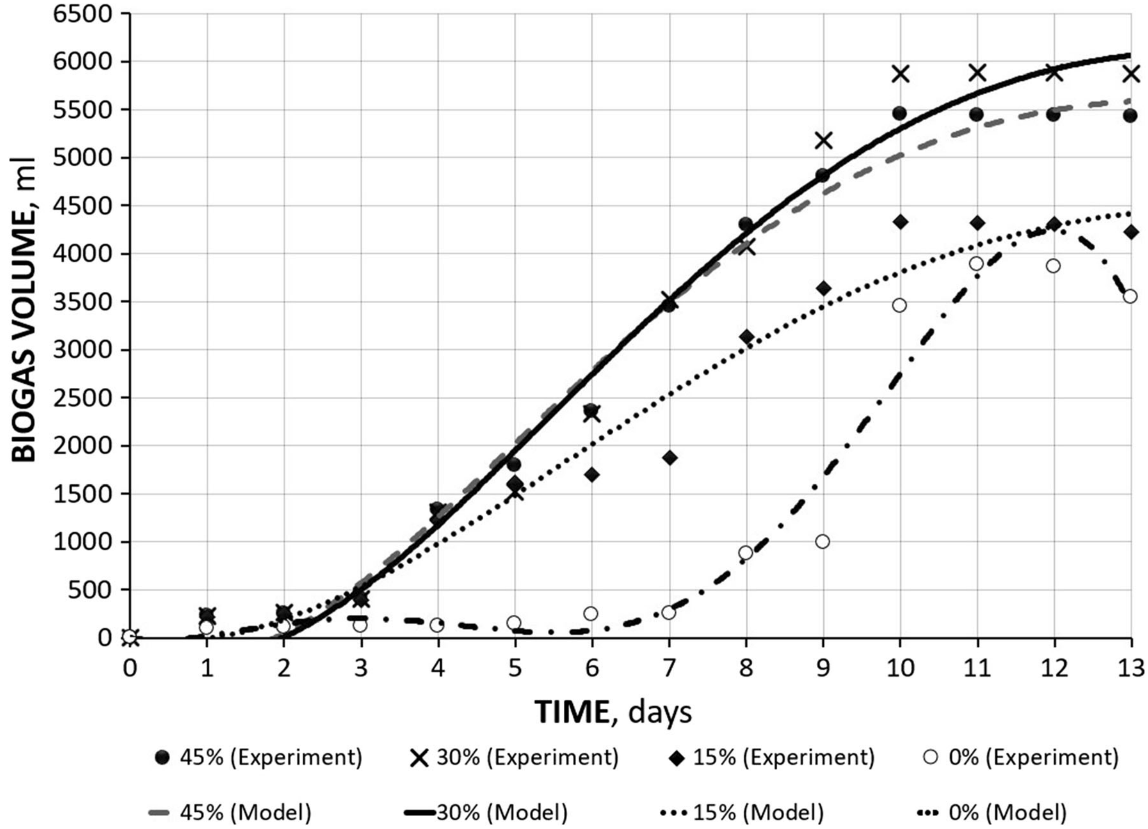

Fig. 5 Experimental rates of biogas yield in the co-digestion of poultry litter with varying amounts of cellulose-containing substrates and comparison to analytical data fitting simulations based on the regression equation

The lag phase was present from the first 3 days for experiments with the addition of co-substrate — dry leaves, and the yield of biogas in the zero samples began within 6–7 days of digestion. The linear phase of gas formation process development in the period from day 6 to 9, with the maximum biogas yield by day 10 with subsequent stabilization at the same level, was quite clearly expressed (5876–5887 ml/day or 326.4–327.0 ml/g DM). In the control version of the experiment, the yield of biogas was equal in value to its yield at the content of the addition of dry leaves of 15% on the DM. The start-up of anaerobic digestion can be carried out with no addition of cellulose-containing substrate, but the start-up time will be longer and the volume of biogas produced would be smaller, which is also confirmed in the research of Czekała et al. [42]. The largest biogas yield was observed with the addition of 30% dry leaves by dry matter. In the process of the control experiment of anaerobic digestion of chicken manure, the remarks to the parameters of technological regimes (temperature, pH, etc.), which caused low productivity of biogas, were revealed. This contributes to the specificity of the component composition of poultry litter, which affects the low activity of methanogens, in particular, it is a consequence of the low ratio of carbon-to-nitrogen content in the processed chicken manure. Thus, according to the research of Kelleher et al. [43], the C:N ratio in the feed was less than 2.0–3.0 leading to an increased ammonia formation during digestion, which inhibited the processes of methanogenesis in the bioreactor.

Hence, the increase of carbon in the dry matter of the raw material naturally led to an increase in the volume of biogas released (while maintaining the C:N ratio greater than 3) and reached its maximum with the addition of dry leaves in the ratio of 30% on the DM. Further increase of cellulose-containing co-substrate did not increase biogas yield.

According to the research of Shapovalov et al. [44], biogas yield varied from 294.0 to 331.7 ml/g DM under anaerobic digestion of chicken manure with 10% of active sludge (Shapovalov Y. B et al. 2019). The production of biogas in the study of Salyuk et al. [45] in solid-phase digestion ranged from 66.2 to 175 ml/g DM, and methane from 11.9 to 72 ml/g DM in mesophilic conditions. Thus, the production of biogas and methane was characterized by high indicators than in the study of Salyuk and co-authors ([45]); 415.46 l of biogas was produced in the substrate of two reactors (100-l volume) for 32 days at 311 K [46]. In the study of Abouelenien et al. [47], methane production was 139.6 ml/g DM at 20% DM content under 328 K. It should be noted that biogas yield is higher under thermophilic conditions. However, based on our experience, in moderate climatic latitudes and with the presence of wintertime, it is important to develop mesophilic technological solutions for the anaerobic digestion of waste, which is economically more reasonable.

The characteristics of the obtained biogas are presented in Table 4.

The concentration of methane varied from 62 to 78% depending on the dose of the cellulose-containing co-substrate. There was also a significant decrease in ammonium yield in experiments with dry leaf additives. It should be noted that without the addition of dry leaves there was more ammonia production, which affected the activity of methanogenic microorganisms and the level of methane production. These results are consistent with other studies on the effect of ammonium on the methanogenesis process (Strick et al. 2006; [48]).

In addition to the intensification of biogas production, the use of co-substrate such as fallen leaves will help to improve the state of urban eco-systems in the direction of sustainable use of this waste.

As can be seen in Fig. 5, the regression modelling nevertheless gave a higher level of correlation with experimental data. The modification of the Gompertz model and the use of the kinetic parameters of the methanogenesis process with the formation of a system of differential levels will enable effective use of these for predicting and optimizing anaerobic digestion, which will be carried out in further studies.

According to the results obtained, it is possible to increase the amount of feedstock, so that the optimal dose of cellulose supplements is taken, and of the opal leaf itself, it is possible to intensify the process of anaerobic digestion of the poultry litter after and change the lag phase in the process.

4 Conclusion

The analysis of the production of poultry waste showed promising growth in the forecast of its formation and high resource potential of using chicken manure for bioenergy purposes. At the same time, it is important to study the processes of co-fermentation of poultry manure with cellulose-containing co-substrate, which has a positive effect on the digestion process and obtaining the best qualitative and quantitative parameters of the resulting bioproducts, such as biogas and digestate.

The problem of finding ways to utilize the dry leaves in urban ecosystems and plant residues in agriculture often remains unresolved. Burning crop residues is the least environmentally sound way to manage this waste. The study on the mineral composition of the leaves of *Acer platanoides L.* showed that the leaves in the mineral composition contain a significant percentage of biogenic elements (Ca, K) which are useful for the development of microorganisms, as well as a significant amount of carbohydrates that can serve as a nutrient medium. In this case, the choice of locations for the selection of dry leaves is important. It is advisable to use cellulose-containing substrates such as leaves with a low level of certain contaminants generated by industrial and transportation activities.

As a result of the study, it was determined that the cellulose-containing co-substrate of dried leaves after preliminary preparation can intensify gas production and reduce the lag phase of the anaerobic digestion of chicken manure. The optimal content of dry leaves was determined to be 30% as its further increase did not lead to significant changes in the indices of the anaerobic digestion process. The linear phase of gas formation process development in the period from day 6 to 9, with the maximum biogas yield by day 10 with subsequent stabilization at the same level, was quite clearly expressed (5876–5887 ml/day or 326.4–327.0 ml/g DM). The regression modelling gave a higher level of correlation with the experimental data. The modification of the Gompertz model and the use of the kinetic parameters of the methanogenesis process with the formation of a system of differential levels will enable the effective use for predicting and optimizing anaerobic digestion.

Further studies will focus on the investigation of different temperature regimes and the effect of changing pH values for the co-digestion process. In addition, experiments will be

Table 4 Composition and properties of biogas

Parameter	Dosage of the co-substrate of dried leaves				
	Without co-substrate	Chicken manure with 15% on DM of the co-substrate of dried leaves	Chicken manure with 30% on DM of the co-substrate of dried leaves	Chicken manure with 45% on DM of the co-substrate of dried leaves	Standard deviation of data
Methane, vol. %	43–50	62–69	70–78	69–76	±0.2
Hydrogen, vol. %	0–1	0–1	0–1	0–1	±0.2
Carbon dioxide, vol. %	32–41	24–38	23–37	29–38	±0.2
Ammonia, ppm	93–108	9–12	4–6	4–6	±0.3

carried out considering large volumes of substrate processing during anaerobic digestion, to study the feasibility of the proposed method.

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