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ORIGINAL PAPER

EVALUATION OF THE CHEMICAL COMPOSITION OF RAW COMMON DUCKWEED (*LEMNA MINOR* L.) AND PULP AFTER METHANE FERMENTATION*

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Abstract

The development of our civilization is associated with an increase in the energy consumption by the general population. Therefore, the energy sector is of strategic importance in the development of modern countries. That is why new technologies and raw materials for the production of renewable energy resources are being widely searched for. The aim of this paper was to assess the efficiency of methane fermentation of common duckweed. Another aim was to assess the chemical composition of substrates intended for methane fermentation and of digestates. Common duckweed biomass, which originated from carp ponds, was subjected to methane fermentation. Moreover, an analysis of the chemical composition of the batch and digestates was carried out. The nitrogen content in the studied samples was determined by the Kjeldahl method, whereas determination of the other elements was based on the ICP-OES method. The research on methane fermentation showed that the amount of biogas obtained from common duckweed is satisfactory. In terms of dry matter of the batch, the total yield of biogas recovered from the batch from common duckweed was higher than that generated by maize silage. Methane fermentation of common duckweed biomass resulted in an increase of most of the studied elements, with the exception of nitrogen. Digestates generated by methane fermentation of common duckweed biomass can be used for supporting plant cultivation, as they contain substantial amounts of calcium, nitrogen and phosphorus. If the studied digestates were applied in a dose of approximately 5 Mg ha^{-1}, the amount of the incorporated calcium would be more than 200 kg Ca. The amounts of nitrogen and phosphorus would amount to 80 and 22 kg, respectively. The content of the other macroelements was lower than specified in the scientific literature for various natural fertilizers. In no case was the threshold heavy metal content for natural fertilizers exceeded in the studied material.

Keywords: common duckweed, methane fermentation, digestates, fertilizer value.

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INTRODUCTION

The primary production level in water reservoirs is very important as it shapes the circulation of basic chemical elements (such as nitrogen and carbon) on a global scale. Due to the constantly increasing demand for food as well as the specific of consumer preference, there has been a constant increase in the consumption of seafood and plant aquaculture products in recent years. While fish production has a negative impact on the natural environment, mollusc and seaweed farming are extremely beneficial for the quality management of the aquatic environments as well as for the use of production space in natural or artificial water bodies. Aquatic plants assimilate biogens occurring in water and use sunlight to build biomass. During a plant life cycle, elements that are built into plants undergo immobilization. However, under natural as well as artificial conditions, once a plant is dead, the decomposition of organic matter leads to oxygen deficit and generates toxic compounds. The removal of aquatic plant biomass is one of the most practical methods to prevent eutrophication of water bodies (Liu et al. 2017). Cultivation of macrophytes is an efficient method to reduce the amount of biogens in water reservoirs (Niemiec et al. 2016, Zhang et al. 2016). Macrophytes that constitute emergent vegetation are characterized by an intensive increase, and their removal from reservoirs poses no technological difficulties. However, more and more often attention is paid to the possibility of using common duckweed or water hyacinth as a factor that reduces eutrophication of natural water bodies or as a medium in the treatment of municipal sewage. Under favourable environmental conditions, the amount of nitrogen fixed by common duckweed was found to be approximately 0.5, whereas the content of phosphorus approximates to 0.1 g m^{-2} day^{-1} (Zhao et al. 2014). Under optimum thermal and light conditions and with a sufficient supply of micro- and macroelements, common duckweed doubles its mass in two days, whereas its annual production may amount to 20-30 Mg ha^{-1} $year^{-1}$ (Duan et al. 2013). These plants fix carbon dioxide more than twice as intensively as the dynamically growing terrestrial energy crops (Muradov et al. 2012). In the Polish climate zone, it is justifiable to use common duckweed. It has a higher growth potential than other aquatic plants and can bioaccumulate heavy metals. This creates an additional opportunity to use duckweed for the treatment of chemically contaminated waters (Goher et al. 2016). However, Oukarroumet (2015) draws attention to the high sensitivity of common duckweed to salinity, which prevents its use in waters receiving runoff effluents from roads and from hard surface areas. An important feature of common duckweed is its ability to adapt to living in a wide range of thermal conditions, which increases chances of using these plants in the temperate climate zone. Common duckweed is a plant with a great potential to be used as food, fodder, fertilizer and a source of energy. As well as showing a high content of protein with beneficial amino acid composition, the plant has a substantial amount of starch and fat (Duan et al. 2013, Godinho et al. 2013).

Using aquatic plant biomass for energy purposes and in plant fertilization is important in the shaping of an environmental protection policy based on more rational use of natural resources. This is particularly important in growing crops that do not supply the soil ecosystem with carbon, such as wheat or oilseed rape (Królczyk et al. 2014). Common duckweed biomass has suitable properties to be used for biochar production (Muradov et al. 2012). Chemical elements present in water or sewage become incorporated into biomass and this process enables their reuse. In conventional sewage treatment facilities, nitrogen compounds are transformed into atmospheric nitrogen, while phosphorus is chemically precipitated and immobilized in sewage sludge. Moreover, sewage treatment is associated with substantial amounts of energy. Using plant biomass for energy production or as fertilizers is also important as regards carbon sequestration (Kostecka, Kaniuczak 2008). An increase in algal biomass at a level of 1 kg dry matter is conditioned by the assimilation of 1.8 kg of carbon dioxide (Pugliese et al. 2015).

The aim of this paper was to assess the efficiency of methane fermentation of common duckweed. Another aim was to assess the chemical composition of substrates intended for methane fermentation and of digestates.

MATERIAL AND METHODS

For the achievement of the research objective, common duckweed biomass from carp rearing ponds located in the commune of Strumień (Poland) was subjected to analysis. The biomass was obtained from filtration screens of the pumping station that supplies fresh water to the first reservoir in a cascade rearing system of one-year old mirror carp. Some of the biomass was obtained by removing duckweed from the surface of the rearing ponds. In the reservoirs studied, duckweed is removed in order to reduce the trophism of water basin. Duckweed was obtained in July 2014 in an amount of 20 kg fresh matter. Then a 2 kg laboratory sample was separated and subjected to chemical analysis. The remaining biomass was subjected to static methane fermentation in a biogas laboratory. In the mass, the moisture content was determined as it is an important parameter for preparing a substrate for methane fermentation. The moisture content of the collected mass was determined using a moisture analyzer. Samples were dried until the mass of the sample was constant, in order to calculate the amount of dry matter (DM) subjected to fermentation (dm_f). Dry matter content in a batch optimally suitable for fermentation is 10%. Proper preparation of biomass batch for a fermenter makes it possible to estimate the amount of emitted biogas of given organic matter. Based on the determined moisture content, the batch mass for fermentation in a 2 dm^3 laboratory fermenter was determined from equation:

$$m_f = \frac{dm_f}{100 - f_m} \cdot 100\ (g)$$

where:

m_f – mass of the fraction (g),
dm_f – dry matter of the fraction subjected to fermentation (g),
f_m – the fraction’s moisture content (%).

A suitable portion of the material was crushed in a laboratory mill, hydrated until reaching a moisture content of about 90%, thus creating optimum conditions for the growth of mesophilic bacteria. A ready batch was placed in a fermentation chamber with the capacity of 2 dm^3 under a controlled temperature environment.

Biogas yield was obtained according to DIN 38414. Fractions were fermented under static conditions, i.e. a batch was placted in a fermentation chamber and the process continued until fermentation was completed. Measurements of the temperature, water, pressure and the amount of biogas obtained were conducted at a test station consisting of a computer station with control software, a water-jacketed chamber with controlled temperature, a variable volume tank for determining the amount of biogas, and a multigas meter BIOTECH70. Throughout the tests, amounts of emitted biogas were recored twice a day, at the same time, from the moment of placing a batch into a fermenter until the end of fermentation. Other parameters of the process, such as the temperature, gas humidity, gas pressure, methane, oxygen, carbon dioxide, and hydrogen sulfide, were saved on a computer hard drive using control and archiving software.

Once the methane fermentation of the investigated material was finished, samples of the solid fraction of the digestates were collected. The content of macroelements (N, P, K, Ca, Mg and Na) and trace elements (Cr, Cu, Fe, Mn, Ni, Pb, Zn and Cd) was determined both in duckweed, which served as batches for the fermenter, as well as in the digestates. The laboratory samples were dried at 65°C, homogenized and subjected to dry mineralization in an open system. The samples were mineralized in a muffle furnace at 450°C. Then they were dissolved in nitric acid solution at a concentration of 20%. An analytical sample contained 3 g dry matter. Concentrations of the elements studied in the solutions were determined by atomic emission spectrometry, on an Optima 7600 spectrometer manufactured by Perkin Elmer. Wavelengths that were used to determine the concentrations of the elements and limits of detection for the applied analytical methods are presented in Table 1. The nitrogen content was determined by the Kjeldahl method using a Kjeltec 2100 distillation unit. The correctness of analyses of the elements was verified by using certified reference material IEA-V-10. Table 1 shows results of analyses of the reference material and an estimated value of recovery based on analyses performed in four replications.

Table 1

Results of analyses of the reference material, recovery value and wavelengths using the ICP-OES method

Parameters	Wavelengths (nm)	Detection limit (mg dm^{-3})	Content in certificated material (mg kg^{-1})	Measured (mg kg^{-1})	Recovery (%)
Mg	285.208	0.0016	1360	1410	103.7
P	213.617	0.076	2300	2205	95.9
Ca	317.933	0.01	21.600	22.260	103.1
Na	589.592	0.069	500	466.5	93.3
K	766.490	-	21.000	20.135	95.9
Cd	228.802	0.0027	0.03	0.033	108.3
Cr	267.707	0.0071	6.5	6.412	98.6
Cu	327.393	0.0097	9.4	9.125	97.1
Fe	238.204	0.0046	185	201.2	108.8
Mn	257.608	0.0014	47	48.56	103.3
Ni	231.604	0.015	4	3.856	96.4
Pb	220.353	0.042	1.6	1.725	107.8
Zn	206.200	0.0059	24	24.62	102.6

RESULT AND DISCUSSION

The study on the fermentation process performed in the laboratory allowed us to assess the sensitivity of the tested fraction to the ongoing biochemical reactions.

Methane fermentation of common duckweed was carried out for thirty days and controlled every day. Starting from the first day of the process, the amount of biogas obtained was increasing. No inhibition of the process was observed. On the fourteenth day, biogas yield exceeded 250 N dm^3 kg^{-1} DM. The total output of gas emitted during the research was at a level of 300 N dm^3 kg^{-1} DM (Figure 1). Figure 2 shows the composition of biogas obtained during methane fermentation from substrate made of common duckweed. Methane yield differed on individual days and was not constant. The highest value of methane was reached on the nineteenth day of methane fermentation: 68% CH_4 (37% CO_2 and 0.4% O_2) – Figure 2. The amount of emitted methane started to decrease afterwards, but the value of the obtained biogas kept increasing slightly. The amount of emitted carbon dioxide differed on individual days. The highest CO_2 content in biogas was 37%. Based on the research carried out, it was found that common duckweed biomass can be successfully used as a batch for methane fermentation. When

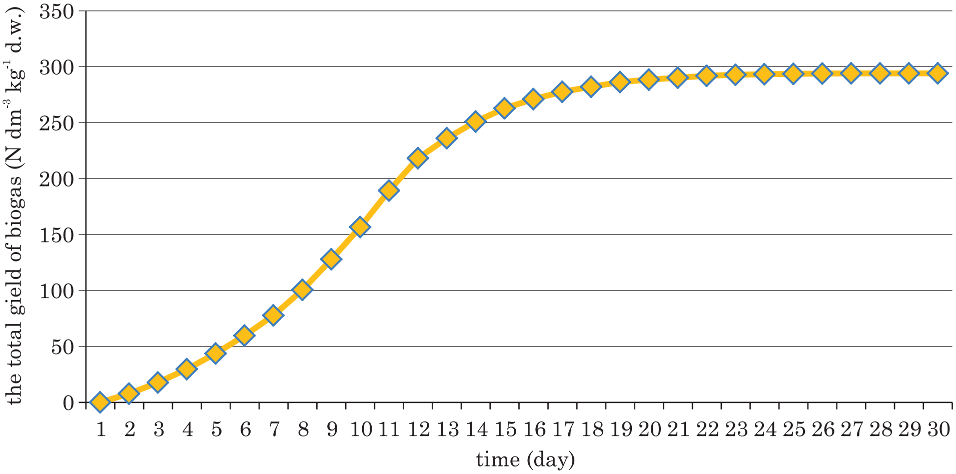

Fig. 1. Total yield of biogas generated from common duckweed fermentation process

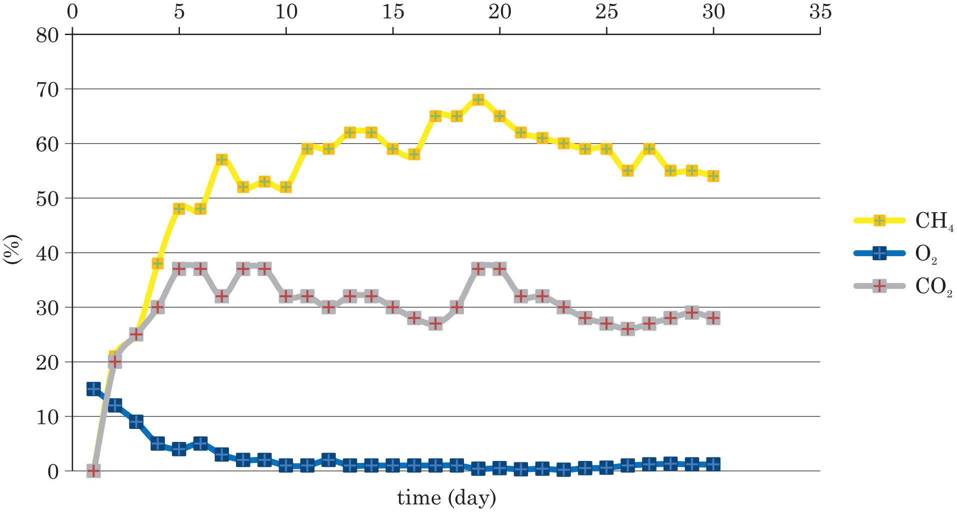

Fig. 2. Chemical composition of gases emitted from common duckweed fermentation

analyzing temporary availability of biomass of common duckweed, this biomass ought to be considered as a co-substrate in agricultural biogas plants. In such a case, the biomass of common duckweed obtained at pumping stations and removed from fish rearing ponds would complement the biogas plant batches because in the plant growing season there is a shortage of maize silage (which is considered to be the basic batch for agricultural biogas plants) on the market. The source literature states that the efficiency of a batch composed of maize silage is at the level of 250 N dm^3 kg^{-1} DM, and the methane content equales 54% (SIKORA 2012).

The nitrogen content in raw duckweed intended for fermentation was 1.62% DM, whereas the amount of this element found in the digestates was 0.834% (Table 2). The fermentation process caused a twofold reduction in the content of this element. Pugliese et al. (2015) observed similar relations in marine algae of the Ulva genus. These authors report that the content of this element in raw algae was at a level of 0.53%, and in the digestates – 0.44%. The research of Bonomo et al. (1996) shows that the nitrogen content in duckweed may fluctuate from 2 to 6% under a high concentration of nitrogen compounds in water. However, such substantial amounts of nitrogen can be found in biomass generated at sewage treatment plants. The plants used in our research came from fish rearing ponds, where the level of biogens in water was relatively low. Weiland (2006) emphasizes that nitrogen presents in fermented organic matter can be better assimilated by plants. That is why using such materials for fertilization ought to be preceeded by studying the trend and the rate of transformations of nitrogen compounds under soil conditions.

Table 2

Content of elements in duckweed and in digestates

Parameters	Unit	Duckweed	Digestates
N	(%)	0.834 ± 0.203	1.626 ± 0.244
P		0.348 ± 0.076	0.443 ± 0.062
K		0.663 ± 0.188	1.306 ± 0.211
Ca		3.723 ± 0.541	4.498 ± 0.608
Na		0.150 ± 0.042	0.262 ± 0.036
Mg		0.317 ± 0.084	0.418 ± 0.063
Cd	(mg kg^{-1})	0.067 ± 0.024	0.116 ± 0.032
Cr		2.232 ± 0.265	2.215 ± 0.498
Cu		1.250 ± 0.321	1.733 ± 0.368
Fe		287.4 ± 36.56	405.3 ± 29.85
Mn		30.78 ± 3.664	30.72 ± 2.981
Ni		1.867 ± 0.135	3.267 ± 0.255
Pb		0.500 ± 0.041	1.525±0.086
Zn		7.617 ± 0.623	10.242 ± 0.714

Phosphorus is the most important chemical element in terms of water eutrophication. Its content in plants removed from water bodies is taken into account in the assessment of the suitability of plants for remediation of water bodies (Zhang et al. 2016, Liu et al. 2017). Recently, the recovery of this element (introduced to water bodies of the hydrosphere) has been a strategic part of new sewage treatment technologies and sustainable aquaculture production. The content of this element in raw duckweed biomass amounted to 0.348% DM, whereas in the digestates it was at a level of

0.44%. The amounts of phosphorus observed in our research were significantly higher than those given by other authors (ZHAO et al. 2014, ZHANG et al. 2016). ZHAO et al. (2014) reported that the phosphorus content in common duckweed biomass ranged from 0.11 to 0.13% DM (Table 2). BONOMO et al. (1996) found that the phosphorus content in common duckweed biomass ranged from 0.2% to 0.3% DM under conditions of a large concentration of this element in water. A very high calcium content was found in the studied material. The concentration of this element in the plant biomass before fermentation was 3.72%. As a result of methane fermentation, the amount of calcium increased and reached 4.498% in the digestate (Table 2). The tested material, both before and after fermentation, had a high potassium content. The amount of this element in the batch was 0.633%, whereas the potassium content in the digestates was at a level of 1.306% (Table 2). Methane fermentation also changed the sodium content. In raw biomass of the studied plants, the amount of this element was at a level of 0.834%, while the level of this element in the digestates raised to 2.615% DM (Table 2). A high content of macronutrients was found in the studied material, at a level observed in manure (XIU et al. 2011, AKBARIAN et al. 2013). Using aquatic plants for sewage treatment as well as creating conditions for their development in polluted water reservoirs constitute a low energy input alternative for sewage treatment by chemical or biological methods using active sediment (GOHER et al. 2016). Using the generated plant biomass for energy purposes is a potentially rich source of renewable energy. On the other hand, the perspective of using methane fermentation waste for crop fertilization enables recirculation of biogenic elements which, under a conventional farming system, would be lost. These three aspects create a wasteless and less emission environmental management system. Chemical elements that mostly determine the fertilizer value of the studied digestates are nitrogen, phosphorus and calcium. Along with the recommended dose of dry matter (5 Mg ha^{-1}) of the studied digestate, approximately 80 kg of nitrogen, 22 kg of phosphorus and over 200 kg of calcium will be introduced. Legally, digestates formed from methane fermentation of common duckweed biomass cannot be regarded as an organic or natural fertilizer due to the lack of repeatability of the chemical composition as well as physical and physicochemical properties. These features make the qualitative standardization of digestates impossible. According to the current law, digestates can be used on farmers' own fields as a soil amendment.

Harvesting aquatic plant biomass is best justified in areas with strong human impact, due to a substantial supply of nutrients. Most often, these are contaminated water bodies in regions of intensive farming or in urbanized and industrialized areas, as well as in the vicinity of bays, ports and estuaries. The removal of aquatic plants from such areas has a verifiable positive effect on the water body's trophism and on the chemical and physicochemical properties of water (PUGLIESE et al. 2015). However, due to the specific character of areas where such plants are collected, there is a real risk of excessive accumulation of trace elements and organic pollutants. Aquatic plants have a unique capacity to accumulate trace elements, which has been pointed out by many authors (Niemiec et al. 2015, Oyuela Leguizam et al. 2017). Plants collected from such areas can have potentially toxic elements at a level rendering them unfit for consumption, fodder or even fertilization purposes. Therefore, before using aquatic plants, their quality should be monitored (Yadav, Chandra 2011). Under conditions of the intensive growth of aquatic plants, a problem of deficiency of some elements, particularly microelements and calcium may arise (Yasee et al. 2016). These authors draw attention to the need of monitoring the level of nutrients in water and in fertilization in order to optimize the primary production in a water body. In our research, the content of nickel, chromium, lead and cadmium in duckweed biomass reached, respectively, 1.867, 2.23, 0.500 and 0.067 mg kg^{-1} DM. As a result of methane fermentation, the amount of nickel, lead and cadmium increased (Table 2). Fermentation also caused an increase in the iron and zinc content in the biomass, while the amount of manganese did not change (Table 2). Critical heavy metal concentrations in organic fertilizers were not exceeded in the studied materials (Regulation 2008). Megateli et al. (2009) report that the heavy metal content in duckweed biomass was several dozen times higher than that observed in our research, which may create problems associated with biomass management. As a rule, biogas production is based on mixtures of co-substrates, which makes is possible to obtain a batch with a desired chemical composition as well as the right physical and physicochemical properties. Duckweed is not often used as a substrate in methane fermentation. Many authors draw attention to considerable differences in the concentrations of proteins, sugars, fat and elements in duckweed depending on the living environment. Variable chemical composition can cause problems in optimizing the parameters of fermentation and its efficiency (Sasmaz et al. 2015). When the chemical composition of algae is variable and there are problems associated with methane fermentation, hydrothermal condensation is a more efficient method for algae processing (Duan et al. 2013).

CONCLUSIONS

1. Methane fermentation of common duckweed biomass resulted in increased amounts of nitrogen, phosphorus, potassium, sodium, calcium, magnesium, cadmium, iron, nickel lead and zinc.

2. A very high calcium content was found in the studied digestates. If this material was applied at a dose of approximately 5 Mg ha^{-1}, the amounts of the incorporated calcium would be more than 200 kg Ca. The levels of nitrogen and phosphorus would reach 80 and 22 kg, respectively.

3. In no case was the heavy metal threshold content for natural fertilizers exceeded in the studied material.

4. The research showed that digestates after methane fermentation of common duckweed biomass can be used to support plant cultivation.

5. The research on methane fermentation showed that the volume of biogas obtained from common duckweed is satisfactory. From the fourteenth day and on, it was 251294 N dm^3 kg^{-1} DM.

6. In the emitted biogas, during the fermentation of the substrate made from common duckweed, the share of 68% CH_4 was recorded, and it is a 15% better result than in the case of maize silage (which is considered to be an optimum batch for agricultural biogas plants).

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