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## STUDY OF THE EFFECT OF BIOCHAR FROM SPENT COFFEE GROUNDS ON ANAEROBIC DIGESTION OF FOOD WASTE FROM THE RESTAURANT INDUSTRY

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### Abstract

The uncontrolled and unsanitary disposal of food waste, which is a valuable raw material for Ukraine's energy independence, has led to a negative impact on the environment, public health and socio-economic development. Integration of food waste into an advanced closed-loop economy will allow for a significant increase in sustainable bioenergy production. The aim of the study was to evaluate the impact of biochar obtained from waste coffee sludge on the anaerobic digestion of food waste from the restaurant industry, which was done using biogas accumulation and digestate quality indicators, such as pH, sCOD, VFAs, NH<sup>4+</sup>-N concentration. The results show that thermophilic anaerobic digestion with a higher degree of hydrolysis was prone to instability due to the accumulation of VFAs and a drop in pH. Biochar from spent coffee sludge effectively stimulates the consumption of VFAs and increases methane production, especially under thermophilic conditions. The biochar treatment achieved both higher maximum specific methane production rates and shorter retention times. As the amount of biochar increased from 0 to 15 g l<sup>-1</sup>, the cumulative methane production under thermophilic conditions increased from 296.7 ml g<sup>-1</sup> VS added to 476.1 ml g<sup>-1</sup> VS added, while the fermentation time decreased from 22 days to 14 days. pH, temperature and VFAs were important factors indicating that increasing the anaerobic digestion process rate leads to better performance in thermophilic digestion using biochar. The potential use of biochar from food waste (waste coffee grounds) in the anaerobic digestion of food waste can simultaneously address the pollution problem of several types of organic waste, including kitchen waste and restaurant food waste. The biochar increased the methane yield and also ensured stable operation with a short lag time in the thermophilic anaerobic digestion process. The methane produced can be used for biomass pyrolysis.

**Keywords:** environmental biotechnology; anaerobic digestion; biogas; biochar; food waste.

## ДОСЛІДЖЕННЯ ВПЛИВУ БІОВУГІЛЛЯ З ВІДПРАЦЬОВАНОЇ КАВОВОЇ ГУЩІ НА АНАЕРОБНЕ ЗБРОДЖУВАННЯ ХАРЧОВИХ ВІДХОДІВ РЕСТОРАННОГО ГОСПОДАРСТВА

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### Анотація

Неконтрольована та антисанітарна утилізація харчових відходів, які є цінною сировиною для енергетичної незалежності України, призвела до негативного впливу на довкілля, здоров'я населення та соціально-економічний розвиток. Інтеграція харчових відходів у розвинену економіку замкнутого циклу дозволить значно збільшити стале виробництво біоенергії. Метою дослідження була оцінка впливу біоcharу, отриманого з відпрацьованого кавового шламу, на процеси анаеробного збродження харчових відходів ресторанного господарства, що була зроблена з використанням показників накопичення біогазу та показників якості дигестату, таких як pH, sCOD, VFAs, концентрації NH<sup>4+</sup>-N. Результати показують, що термофільне анаеробне збродження з вищим ступенем гідролізу було схильне до нестабільності через накопичення ВЖК і падіння pH. Біовугілля з відпрацьованого кавового шламу ефективно стимулює споживання VFAs і збільшує виробництво метану, особливо в термофільних умовах. Під час обробки біологічним вугіллям були досягнуті як максимальні питомі показники виробництва метану,

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так і скорочення часу затримки. Зі збільшенням кількості біопалива з 0 до 15 г·л<sup>-1</sup> кумулятивне виробництво метану в термофільних умовах зросло з 296.7 мл·г<sup>-1</sup> VSadded до 476.1 мл·г<sup>-1</sup> VSadded, а час зброджування скоротився з 22 днів до 14 днів. рН, температура і VFAs були важливими факторами, які вказували на те, що збільшення швидкості процесу анаеробного зброджування приводить до кращої продуктивності в термофільному зброджуванні за допомогою біопалива. Потенційне застосування біовугілля з харчових відходів (відпрацьована кавова гуща) в анаеробному зброджуванні харчових відходів може одночасно вирішити проблему забруднення декількох видів органічних відходів, включаючи кухонні відходи та харчові відходи ресторанного господарства. Біовугілля збільшило вихід метану, а також забезпечило стабільну роботу з коротким часом затримки в процесі термофільного анаеробного зброджування. Утворений метан може бути використаний для піролізу біомаси.

*Ключові слова:* екологічна біотехнологія; анаеробне зброджування; біогаз; біочар; харчові відходи.

## Introduction

The problem of waste disposal is global in nature, with more than 3500 million tonnes of food waste produced annually worldwide, a significant amount of which is not used for its intended purpose and ends up in landfills [1–3]. One of the valuable resources that can be further used as secondary raw materials is food waste, which can be used to produce a range of useful materials, such as biogas, biofertilisers, bioethanol, biodiesel, vinegar, pigments, lactic acid and antioxidants. The composition of food waste from private households is similar to that of food waste from hotel and restaurant complexes, which can include leftovers, fruits, vegetables, bread, dairy products, and various cooking wastes [4].

Vegetable residues are commonly reused in the food industry, composted to produce vermicompost and fermented into biogas. This is due to the fact that they contain proteins, polysaccharides (starch, cellulose, hemicellulose and lignin), organic acids, oils/lipids, and trace elements (potassium, phosphorus, nitrogen, etc.), and the moisture and total solids content is 70–80 % and 20–30 %, respectively [2; 5].

When comparing anaerobic digestion (AD) with classical methods of waste treatment or disposal (composting, incineration, landfilling, storage in open dumps), the cost-effectiveness and alternative to the existing management of urban organic waste is clearly visible, i.e., the reduction of waste produces biogas and biofertiliser, which reproduces the concept of reuse of resources with their conversion into bioenergy [6; 7].

Biogas production reduces methane emissions into the atmosphere, which helps to reduce the impact of human activity on the planet's temperature, given that methane has a 21 times stronger negative impact than carbon dioxide (CO<sub>2</sub>). According to previous studies, one of the most important factors in the formation of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) is food waste accumulating in landfills, for example, in 2020, in May, the highest value of greenhouse gases in the entire history of observation was

recorded, which was 417 ppm [2; 8; 9].

Food waste with a high concentration of carbohydrates, proteins and low lipids is favourable for biogas production due to the high hydrolysis rate of hydrocarbons and proteins [5]. The lipid content of fruit and vegetable waste is significantly low, but high in kitchen waste. It has been observed that the total lipid content of fruits and vegetables was 11.8 % of the total kitchen waste content of 21.6 % [10; 11]. Lipids have a high conversion efficiency to methane and a low microbial value added [12].

Despite the benefits of recycling, the technical requirements for fermentation are quite high, especially when it comes to separating food waste from materials that are not suitable for fermentation (bones, glass, plastic packaging, etc.).

Temperature plays an important role in the anaerobic digestion process. In thermophilic conditions, food waste is enriched with thermophilic or thermophilic-tolerant microbes for co-digestion, which provide degradation of organic matter, hydrogen transfer and maintain process stability. Under mesophilic conditions, the main methanogens include Methanosaeta, Methanosarcina, Methanococcus, Methanospirillum, Methanolinea, Methanobacterium, Methanobrevibacter, while at thermophilic temperatures, some specific communities are selectively enriched, such as Methanosarcina thermophila, Methanothermobacter thermophilus [13].

To maximise biogas yields through anaerobic degradation of food waste, animal manure (pigs, cattle and sheep) is added to increase the amount of biogas due to methanogenic bacteria in animal manure [14].

A number of studies have used different food waste as a substrate in different proportions (tomato pulp, grape pulp and olive pulp together with animal manure), in all experiments the addition of manure increased the amount of biogas produced and the higher the manure content, the faster the biogas production. Fruit and vegetable residues have a high moisture content of biodegradable organic matter that can

be used for biogas production, e.g. cabbage residues produce 0.23 m<sup>3</sup> of methane per 1 kg of volatile solids, tomato seeds and peel 218 litres of methane per 1 kg, corn residues 317 litres of methane per 1 kg, and tea residues 385 m<sup>3</sup> per 1 tonne of volatile solids [15; 16].

Studies were conducted in three parallel at the temperature (55 °C) of a reference biogas plant for 33 to 37 days (depending on the amount of biomethane produced), samples of substrate, digestate and homogeneous mixtures were collected from an industrial-scale biogas plant, and the sand content of different substrate streams was determined to design an experiment on the effect of sand content on biomethane production efficiency. Analyses were performed: total solids (TS), volatile solids (VS) and pH analyses for the substrate, digestate and test samples. In other studies, it was found that by increasing the SRT from 30 days to 50 days, the TS concentration increased from 43 g/l to 56 g/l, due to the reduction of VS and increase in biogas yield, the process performance increases, which can be explained by the change of microbes and better passage of the hydrolysis stage [17].

In addition to food waste, various variations of organic waste are often used as a substrate, for example, anaerobic digestion of wheat straw and other agricultural waste with wastewater with the integration of a bioelectrochemical reactor at different voltages was investigated. The following parameters were considered: HRT, organic loading rate, and supply voltage, where methane production was maximum (16.349.17 ± 15414 mL), a bioelectrochemical digester operating at 40 mV was used. Different voltages also significantly increased the COD removal rate, which was the highest (175.17 ± 81.39 ml g<sup>-1</sup>) at 40 mV [18].

To optimise and improve the anaerobic degradation process, carbon-rich materials are used to increase biogas yields, one of which is biochar, which is obtained as a result of the thermochemical conversion of biomass waste [19], it is a granular solid that is stable and has a microporous structure with a large surface area [20]. Biochar can be produced in large quantities and relatively cheaply [21], and a wide range of organic waste is used as a feedstock for biochar, such as coffee grounds [22] or citrus peels [23].

The pyrolysis of coffee grounds in the temperature range from 200 to 850 °C and treatment with various reagents can produce biochar with different properties [22]. Thermal treatment at 850 °C for a time with a limited O<sub>2</sub>

content (20 %), by carbonisation, produced biochar, the mass of which consisted mainly of carbon and oxygen, and the presence of a small amount of other minerals was also noted. The biochar after treatment increased the pore volume to 0.238 ml/g, of which 0.177 ml/g corresponds to micropores, and the total micropore surface area was 379 m<sup>2</sup>·g<sup>-1</sup> [22].

The use of biochar in anaerobic digestion increases the process performance and the amount of biogas produced due to increased buffering properties, ammonia acid inhibition by biochar, and improved microbial enrichment [19; 24; 25].

Given that the thermal conditions of the process strongly influence anaerobic digestion, it should be noted that the use of biochar can increase cumulative methane production by about 20 % and reduce the accumulation of VFAs under mesophilic conditions [26]. It has been shown that under thermophilic conditions, a 1.8-fold increase in biogas production was observed [27].

The aim of the study was to evaluate the effect of biochar obtained from spent coffee sludge on the processes of anaerobic digestion of food waste from the restaurant industry using biogas accumulation and digestate quality indicators, such as pH, sCOD, VFAs, NH<sub>4</sub><sup>+</sup>-N concentration.

To achieve this goal, we need to solve the following tasks:

- to study the effect of biochar on the cumulative methane production as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions;
- to study the effect of biochar on the pH of the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions;
- to study the effect of biochar on the sCOD of the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions;
- to study the effect of biochar on the accumulation of NH<sub>4</sub><sup>+</sup>-N in the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions;
- to study the effect of biochar on the accumulation of VFAs in the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions.

## **Material and Methods**

*Raw materials.* The raw material used was

food waste from the Zucchini restaurant (Odesa, Ukraine), which was collected during three working days of the restaurant during the summer season of its operation, and impurities that were not suitable for anaerobic digestion, such as bones, were removed. The treated food waste was ground in a meat grinder and stored at  $-20\text{ }^{\circ}\text{C}$  in glass containers. The initial chemical parameters of the food waste were as follows: pH 6.1, total solids (TS)  $18.4 \pm 0.3\%$ , volatile solids (VS)  $17.9 \pm 0.3\%$ , protein content  $4.0 \pm 0.2\%$ .

In order to accelerate and improve the methane digestion process, the substrates MT (a mixture of food waste (FW) and cow manure (CM) when digested in a mesophilic temperature regime in a weight ratio of 2:1) and TT (a mixture of food waste (FW) and cow manure (CM) fermented in a thermophilic temperature regime in a weight ratio of 2:1) were pre-incubated in a reactor for 5 days, followed by the addition of food waste. Biochar was added to the separately prepared control groups MT and TT,

resulting in two more groups MT with 5, 10 and 15 percent biochar content, and TT with 5, 10 and 15 percent biochar content.

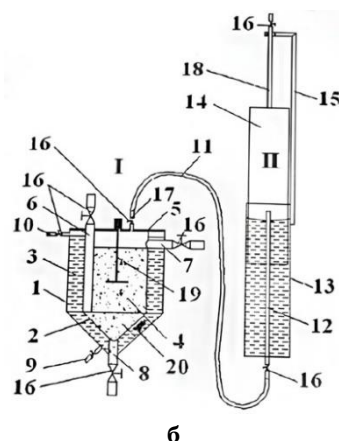
The inoculum was obtained from a laboratory anaerobic reactor in which a mixture of FW and CM was processed. Its chemical parameters are as follows: pH 8.1, total solids (TS)  $43.0 \pm 2.8\text{ g l}^{-1}$ , volatile solids (VS)  $16.0 \pm 2.5\text{ g l}^{-1}$ , chemical oxygen demand (sCOD)  $360\text{ mg l}^{-1}$ .

*Characteristics of biochar.* The biochar was obtained from waste coffee grounds by pyrolysis at  $300\text{ }^{\circ}\text{C}$  for 1 hour, using sulfamethoxazole (SMX) as a decomposition catalyst by activation with persulfate. The surface area studied by the Brunauer-Emmett-Teller (BET) method was  $45\text{ m}^2\text{ g}^{-1}$ , and the main pore size was 14 nm.

*Experimental installation and operation of the reactor.* The research was carried out on a laboratory biogas plant BP-1 of the UASB type with a volume of  $76.8\text{ m}^3$ , in which all four stages of methane formation took place (Fig. 1).



a



b

Fig. 1 - a - biogas laboratory plant (BP-1) type UASB; b - schematic diagram of a biogas plant of the UASB type

The BP-1 consists of a methane digester, where methane fermentation takes place, and a gas holder for biogas accumulation. An important element of the plant is a device for heating and mixing the substrate. The digester I consists of an outer 1 and an inner 2 body, between which there is a water jacket 3 - a container filled with water through a pipe 9 and used to transfer heat from the heater 20 to the substrate. When water is poured into the water jacket, air is removed through pipe 10 and valve 16. To create a tightness of the core of the digester 4, it is covered with a lid 5 with a seal. The substrate is introduced into the active zone of the digester 4 through pipe 6. The pipe 6 reaches almost to the bottom of the active zone of the bioreactor 4, so a fresh part of the substrate is fed into the lower part of the reactor active zone, thereby displacing

the biomass that has fermented through the pipe 7. To drain all the biomass, pipe 8 is used. To prevent crusting and to ensure biomass homogeneity, stirrer 19 is used to periodically mix the biomass in the reactor core. The biogas from the reactor is fed through pipe 17 to gas pipeline 11 and then to gas holder II via pipe 12. In this installation, a "wet" gas holder is used, which consists of two cylindrical containers: a body 13 and a level gauge cylinder 14, as well as a guide 15. The body of the gas holder 13 is filled with water, in which the empty level gauge cylinder 14 floats like a float. Biogas enters the internal cavity of the level gauge cylinder 14 through the pipe 12, which, when filled with biogas along the guide 15, rises above the gas holder body, which in turn allows determining the presence and volume of gas in the gas holder.

The reactors were loaded to 2/3 of their capacity. The mixtures were moved and humidified daily to keep the moisture level at approximately 80 % for 20–25 days, and during the process, approximately 5 g samples were taken each day

to study the process [28]. The reactors were isolated, and the influence of ambient temperature on the data obtained is not taken into account. Each study was conducted in triplicate.

Table 1

Experimental conditions used in this study			
Treatment	Temperature (°C)	Biochar, %.	Substrate
Mesophilic treatments			
MT	35	-	FW + CM
MB5	35	5	FW + CM
MB10	35	10	FW + CM
MB15	35	15	FW + CM
Thermophilic treatments			
TT	55	-	FW + CM
TB5	55	5	FW + CM
TB10	55	10	FW + CM
TB15	55	15	FW + CM

**Analytical methods.** The dry matter content and organic dry matter content were determined by the method based on the determination of the mass of the material before and after drying at 100-105 °C and 500 °C [29; 30]. A BZH Series BZH-12-10 muffle furnace was used. Chemical oxygen demand: 5220 D, closed reflux, colourimetric method [29].

## Results and Discussion

**Study of the effect of biochar on the cumulative methane production as a result of anaerobic digestion of food waste in mesophilic and thermophilic conditions.** The monitoring and control of anaerobic digestion processes based on physicochemical parameters (defined as routine process monitoring and control) has the following limitations: 1) there are no generally

accepted early warning indicators and monitoring of physicochemical parameters cannot predict future performance and stability; 2) only a few parameters can be monitored on-line, which weakens the timeliness of process diagnosis; and 3) process control is a corrective measure that is difficult to implement successfully. Process optimisation is, therefore, a challenging task. The cumulative methane production from anaerobic digestion of food waste in the presence of biofuels has been studied under mesophilic and thermophilic conditions.

The cumulative methane formation as a result of anaerobic digestion of food waste and spent activated sludge in the presence of biofuels under mesophilic conditions is shown in Fig. 2.

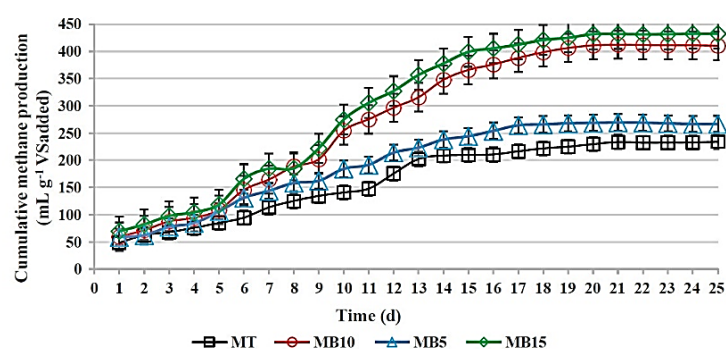


Fig. 2. Changes in cumulative methane production during mesophilic treatment. Error bars indicate the standard errors of the ternary reactors

Under mesophilic conditions, the cumulative methane production in the groups with the addition of biofuels MB5, MB10 and MB15 was 266.8 ml g<sup>-1</sup> VS added, 410.3 ml g<sup>-1</sup> VS added, 432.6 ml g<sup>-1</sup> VS added, while in the control group (MT), a cumulative methane production of 234.0 ml g<sup>-1</sup> VS added was observed. The results indicate that biofuels significantly increased

methane production. The addition of 5 % biochar increased biogas production by 14 %, the addition of 10% biochar to the substrate increased biogas production by 75.3 %, and the substrate containing 15 % biochar led to an increase in biochar production by 84.9 %. Such a significant improvement is likely due to an increase in the rate of hydrolysis or solubilisation of food waste

as the rate-limiting step in mesophilic digestion. As a result of the addition of biochar, the methanogenesis step was probably balanced with the acetogenesis step to cooperate to produce methane without significant inhibition, and biochar played a significant role in anaerobic digestion. Regarding the daily methane production, all groups reached a peak of 48.5 ml g<sup>-1</sup> VS added, 58.7 ml g<sup>-1</sup> VS added, 59.3 ml g<sup>-1</sup> VS added and 69.4 ml g<sup>-1</sup> VS added on day 1. After that, the daily methane production rate decreased sharply due to the rapid consumption of soluble substrates, especially for the MT group. According to the results of the study, it can be stated that the substrate mixtures

with the addition of biochar recovered quickly and reached the second peak of methane production on day 5 with a value of 29.9–33.2 ml g<sup>-1</sup> VS added, while the MT group reached the second peak on day 12 with a value of 24.5 ml g<sup>-1</sup> VS added. According to the results of experimental studies, with an increase in the dose of biochar, the daily rate of methane formation also increases significantly. A similar trend was observed in the third peak of daily methane production.

The cumulative methane formation as a result of anaerobic digestion of food waste and spent activated sludge in the presence of biofuels under thermophilic conditions is shown in Fig. 3.

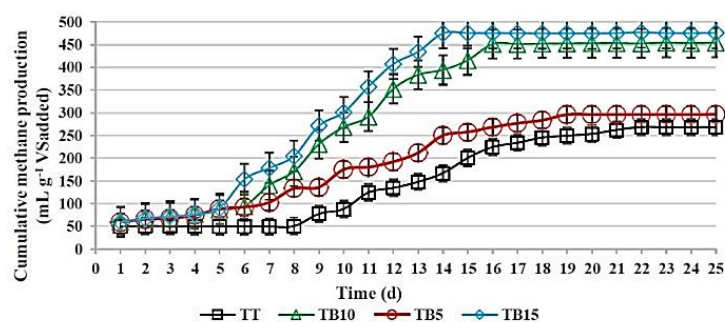


Fig. 3. Changes in cumulative methane production during thermophilic treatment

Methane production showed a significant difference under thermophilic conditions (Fig. 3) compared to mesophilic conditions. In the TT group, the cumulative methane production reached a stable level of about 268.8 ml g<sup>-1</sup> VS added after 22 days, which was about 16 % higher compared to mesophilic conditions. At higher temperatures, anaerobic digestion probably led to a greater hydrolysis or solubilisation of FW and a further increase in methane production. For the biofuel-added groups, the cumulative methane production reached 296.7, 454.5 and 476.1 ml g<sup>-1</sup> VS added in TB5, TB10 and TB15, respectively. Furthermore, the corresponding time for complete fermentation was 19 days, 16 days and 14 days, respectively. Compared to TT, the methane production increased by 10.4 %, 69.1 % and 77.1 %, and the fermentation time was reduced by 13.6 %, 27.3 % and 36.6 %, respectively. The results indicate that biofuels had a positive impact on increasing methane production and reducing lag time. In terms of daily methane production, three peaks were also observed for all groups. The first peak occurred on day 1, with higher methane production in the biofuel group (59.3–60.0 ml·g<sup>-1</sup> VS added) compared to the control group (49.3 ml g<sup>-1</sup> VS added). This was followed by a stagnation period

of 6, 5, 4 and 3 days for TT, TB5, TB10 and TB15, respectively. The stagnation can be explained by the higher temperature, higher hydrolysis rate and accumulation of VFAs, which inhibited the activity of methanogens. The biofuel-treated TB15 group initially resumed methane production and reached a second peak at 63.6 ml g<sup>-1</sup> VS added on day 6, followed by TB10 on day 7 and TB5 on day 9. In addition, the peak of daily methane production was observed after 2–3 days and then quickly stabilised. In contrast, the TT of the control group was relatively weaker in daily methane production even after prolonged stagnation. The maximum daily methane production in the TT was only 19.7 ml g<sup>-1</sup>. These results confirmed that the thermophilic anaerobic digestion improved the methane production rate and the biochar from waste coffee sludge was effective in further maintaining the improved and stable performance of the methane digestion process.

*The study of the effect of biochar on the pH of the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic substrate pH conditions is an important parameter that determines the stability of the anaerobic digestion process.*

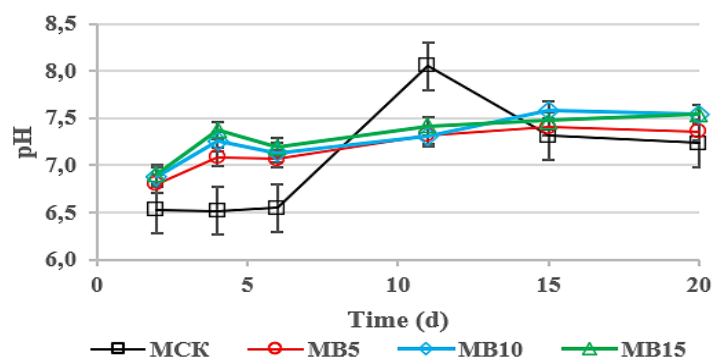


Fig. 4. Changes in pH during mesophilic treatment

As shown in Fig. 4, in the mesophilic treatment, the pH was low and decreased at the early stage of anaerobic digestion (day 1–5), then fluctuated over time and finally stabilised at about 7.5 in the MT group. In the groups receiving biochar, the pH of the substrate containing biochar gradually increased with increasing dose of biochar in all

treatments and stabilised at about 7.7 for MB5 and MB10, and about 7.8 for MB15, indicating a high buffering capacity of biochar.

As for the thermophilic treatment (Fig. 5), the pH fluctuations were much greater than in the mesophilic treatment.

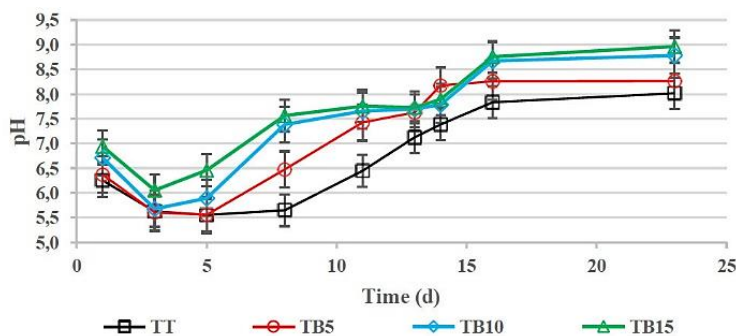


Fig. 5. Changes in pH during thermophilic treatment

The pH of thermophilic treatment gradually decreased from 6.25 on day 1 to 5.55 on day 5 in the TT group. The rapid acidification in TT indicates that the high temperature accelerated the hydrolysis rate and methanogens did not multiply to convert VFAs rapidly, resulting in the accumulation of a large amount of VFAs and a rapid decrease in pH. After a certain period of delay, the pH gradually increased. Already on the 15th day of incubation, the pH value in the sample with the highest biochar content reached a plateau with a pH of 8.96, for TB10 – 8.78, for TB5 – 8.26. This was due to the fact that the methanogens gradually restored their activity and continuously converted the VFAs, and the pH increased to a level suitable for anaerobic digestion. pH in the biochar groups (TB5, TB10 and TB15) was initially higher than in the control group, and the higher the dose of biochar, the higher the pH values. This is due to the fact that alkaline biofuels can neutralise VFAs. In addition, the biofuel-containing groups can also prevent

the pH from dropping rapidly in the initial stage and recover quickly after acidification. Compared to mesophilic anaerobic digestion, biochar has a higher buffering capacity against the pH of the system under thermophilic conditions, thereby reducing the negative impact of VFAs on anaerobic digestion.

*Study of the effect of biochar on the sCOD of the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions.* Despite the ever-growing interest and popularity, large-scale anaerobic digesters typically operate at low organic loading rates (OLR), from 1 to 4 g VS L<sup>-1</sup> d<sup>-1</sup>, or with long hydraulic retention times (HRT), up to 80 days. This results in low biogas production, which reduces the efficiency and economic viability of the process. Increasing the OLR (hydraulic or organic load) can help to increase gas production and improve process efficiency, but instability during continuous operation of the AD is a major problem.

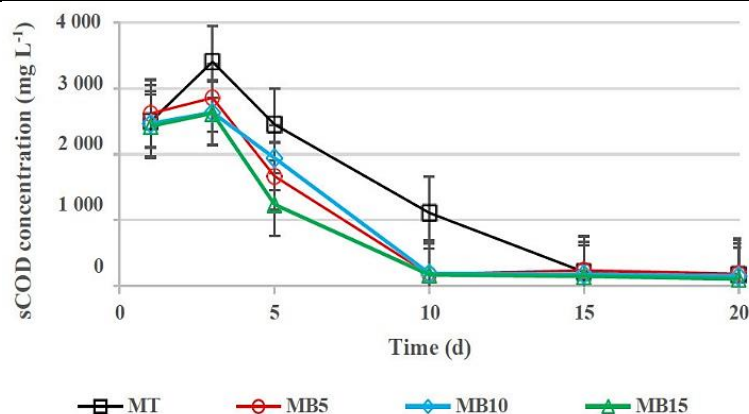


Fig. 6. Changes in sCOD during mesophilic treatment. Error bars indicate the standard errors of the ternary reactors

The change in the sCOD concentration under different modes is shown in Fig. 6. At the initial stage, the sCOD concentration in all treatments was similar and ranged from about 2589–2652 mg l<sup>-1</sup>, and in the groups where biochar was used, the sCOD concentration was slightly lower, probably due to its adsorption capacity. On day 3, the sCOD concentration increased to a high level,

especially in the MT group. The COD concentration then gradually decreased to 107–162 mg·l<sup>-1</sup> with digestion time. Among these treatments, COD concentrations decreased faster with higher doses of biochar, confirming the effectiveness of biochar in improving organic matter decomposition.

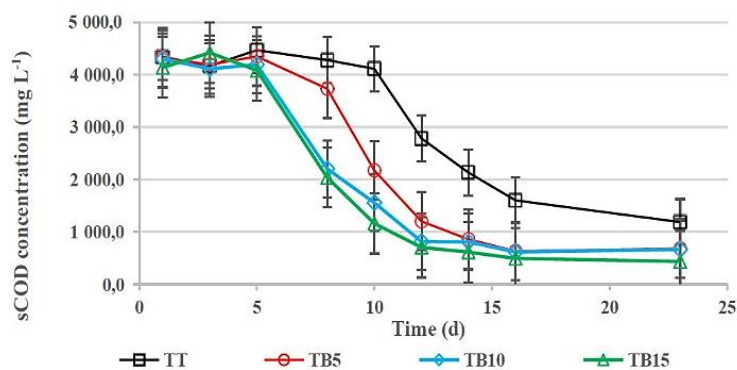


Fig. 7. Changes in sCOD during thermophilic treatment

Similarly, the sCOD degradation trend for thermophilic treatment (Fig. 7) was comparable to that for mesophilic treatment. The main difference is that biochar is more effective at higher doses for sCOD degradation. In addition, the initial and final sCOD concentrations under thermophilic conditions were much higher than under mesophilic conditions. This confirms that thermophilic treatment achieves a higher rate of hydrolysis or solubilisation of FW, which ultimately improves methane production.

Pretreatment and co-digestion are common methods for reducing ammonia in substrates. In addition, dilution, struvite precipitation, stripping, membrane technology and ion exchange are commonly used to remove ammonia

in digesters. Among these, pretreatment and co-digestion are expensive and complex, while dilution and precipitation reduce the effective space in the reactors, resulting in lower OLR. For effective ammonia removal by evaporation, it is necessary to increase the pH of the wastewater to 10-11 and to ensure a constant flow of heat and/or gas.

*Study of the effect of biochar on the accumulation of NH<sup>4+</sup>-N in the reaction mixture (digestate) as a result of anaerobic digestion of food waste under mesophilic and thermophilic conditions.* It is known that the relatively high protein content of food waste is accompanied by a possible inhibition of anaerobic digestion by ammonia.



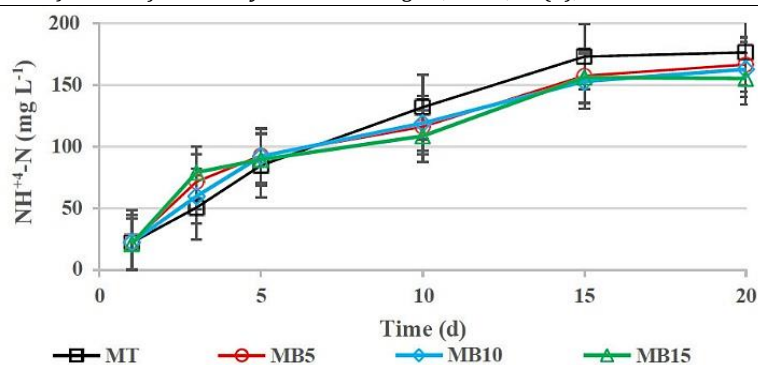


Fig. 8. Change in NH<sup>4+</sup>-N during mesophilic treatment

In the study under mesophilic conditions, an increase in NH<sup>4+</sup>-N was observed (Fig. 8), since the destruction of VFAs in anaerobic digestion is accompanied by the formation of NH<sup>4+</sup>-N. In the

substrates where biofuels were used, the concentration of NH<sup>4+</sup>-N was lower than in the control groups, which is probably due to the adsorption capacity of biofuels.

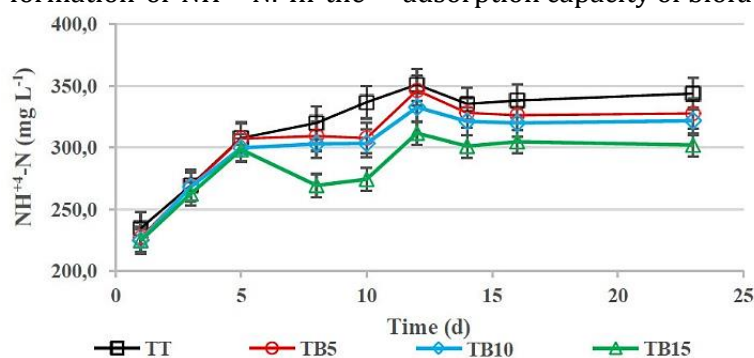


Fig. 9. Change in NH<sup>4+</sup>-N during thermophilic treatment

As follows from the experimental data, thermophilic treatment (Fig. 9) leads to accelerated adsorption of NH<sup>4+</sup>-N, which is accompanied by a significantly lower concentration of NH<sup>4+</sup>-N in TB10 and TB15.

*Study of the effect of biochar on the accumulation of VFAs in the reaction mixture (digestate) as a result of anaerobic digestion of food*

*waste under mesophilic and thermophilic conditions.* VFAs are important intermediate products, the formation of which is explained by deviations in the normal course of the methanogenesis process, and are also a certain indicator of the stability of methane digestion (Figures 10, 11).

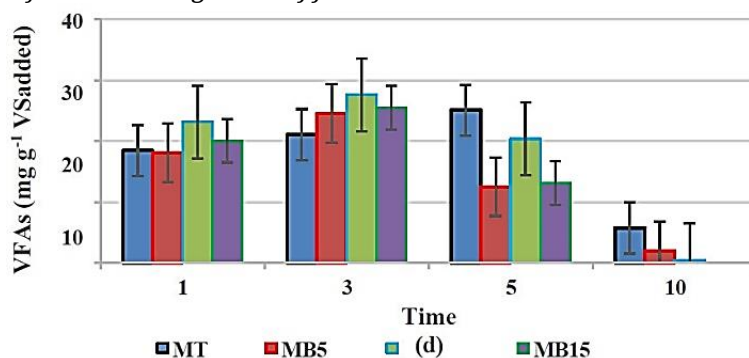


Fig. 10. Changes in VFAs during mesophilic treatment

At the initial stage of anaerobic digestion without biofuel, as shown in Fig. 10, the concentration of TFA in the control group under mesophilic treatment increased from 19.3 ml g<sup>-1</sup> VS added on day 1 to 25.8 ml g<sup>-1</sup> TFA on day 4, while the concentration of TFA in the thermophilic groups

receiving thermophilic treatment (Fig. 11) increased approximately 2.2-fold, from 17.4 ml g<sup>-1</sup> TFA on day 1 to the highest level of 41.3 ml g<sup>-1</sup> of higher fatty acids on day 7. In the mesophilic biochar treatment groups, more SFAs were accumulated than in the control group,

reaching a maximum on day 2. The maximum concentration of VFAs was observed in the MB10 group – 29.7 ml g<sup>-1</sup> VSadded.

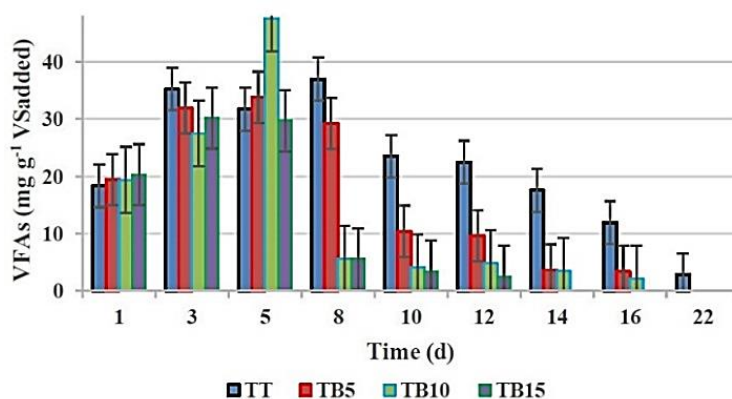


Fig. 11. Changes in VFAs during thermophilic treatment

Similarly to the mesophilic treatment, the biochar groups are characterised by a significant increase in FFA utilisation at higher doses of biochar in the thermophilic treatment regime (Fig. 11). In addition, the groups with biochar achieved the highest level of FFA accumulation – 49.1 ml g<sup>-1</sup> VSadded in the TB10 group.

### Conclusions

In this study, a comprehensive assessment of the effect of biochar obtained from waste coffee grounds on the mesophilic and thermophilic anaerobic digestion of food waste from the restaurant industry was carried out, and the mechanism of this effect was identified.

The results show that thermophilic anaerobic digestion with a higher degree of hydrolysis was prone to instability due to the accumulation of VFAs and a drop in pH. Biochar from spent coffee sludge effectively stimulates the consumption of VFAs and increases methane production, especially under thermophilic conditions. The biochar treatment achieved both higher maximum specific methane production rates and

shorter retention times. Biocarbon significantly improved methane production in the thermophilic anaerobic digestion of food waste, reducing the accumulation of VFAs, and recovering quickly from low pH. As the amount of biofuel increased from 0 to 15 g·l<sup>-1</sup>, the cumulative methane production under thermophilic conditions increased from 296.7 ml g<sup>-1</sup> VSadded to 476.1 ml g<sup>-1</sup> VSadded, while the fermentation time decreased from 22 days to 14 days. pH, temperature and VFAs were important factors that indicated that increasing the anaerobic digestion process rate leads to better performance in thermophilic digestion with biofuel. A 13.6–36.6 % reduction in digestion time means that the reactor can process 20 % more liquid and solid food waste, which saves significant costs. With further optimisation of the operating parameters, such as pre-treatment and increased biomass loading rates, much more methane can be generated, which will significantly increase profitability.

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