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Enhancing anaerobic digestion of automotive paint sludge through biochar addition

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ABSTRACT

The reduction of traditional fuel sources and the unpredictability of the global economy have led to a push for renewable energy alternatives. Waste recycling can significantly reduce greenhouse gas emissions. In this study, the effects of different proportions of biochar on the efficiency of mesophilic anaerobic digestion of automotive paint sludge were investigated over a period of one month. A combination of paint sludge and anaerobic sludge in a ratio of three to one was used, and biochar was added to the anaerobic digestion reactor in two different amounts of 10 and 26 g/l, with a control sample without biochar. The cumulative volume of biogas produced at the end of the one-month experiment was recorded for three samples: the control sample (without biochar), the second sample (with 2 g of biochar), and the third sample (with 5.2 g of biochar). The volumes of biogas produced were 300, 380, and 530 ml, respectively. Additionally, the COD reduction rates were 25%, 33%, and 48%, and the VS decrement rates were 21%, 27%, and 43%, respectively. The findings showed that adding biochar to the anaerobic digestion reactor containing automotive paint sludge increased biogas production. Additionally, gas chromatography results for an optimal sample of biogas extracted from the anaerobic digestion reactor indicated the presence of about 50% methane gas. These results highlight the potential for utilizing biochar in anaerobic digestion processes to improve renewable energy production and waste management.

1. Introduction

Despite the increasing costs of energy, there is a surge in demand for new automobiles, resulting in a significant expansion of the automotive industry [1,2]. Researchers have identified the painting process as the primary source of hazardous waste in the automotive industry, accounting for 60–80% of environmental concerns for vehicle manufacturers [3–12]. Improper management of paint sludge, a by-product of the process, can have severe consequences for the environment, including soil and water contamination [13]. The negative impact of paint sludge is not limited to human health, but also extends to local flora and fauna [14]. For example, a manufacturer producing 400,000 vehicles annually could generate up to 410,000 m^3 of wastewater with a mean chemical oxygen

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Table 1
Main characteristics of produced biochar.

Parameter [Unit]	Value
V_m [cm^3 (STP) g^{-1}]	0.3081
$a_{s,BET}$ [m^2 g^{-1}]	1.3412
C	43.292
Total pore volume ($p/p_0 = 0.990$) [cm^3 g^{-1}]	0.009855
pH	8.0
Mean pore diameter [nm]	29.392

demand (COD) value of 11.4 kg/m^3, primarily from the paint and emulsion parts [1]. Effective waste management is crucial to mitigating the harmful effects of hazardous waste in the automotive industry, particularly in relation to the paint process [1]. In conventional vehicle factories, wet paint-spraying processes typically result in only 50–80% of the paint being delivered to the automobile, with the remaining 20–50% transferred by the paint shop's air stream and recirculating water wash [15]. Paint sludge is composed of various organic solvents and water [6] and is classified as hazardous waste under the EU waste classification code 080113. In the automotive industry, paint sludge is the most significant type of waste generated during painting operations, with each painted automobile generating 1.5–5.0 kg of solvent- or water-based paint sludge [7].

The demand for automotive paint has led to growing concerns about the negative impact of volatile organic compounds (VOCs) [6]. Reports indicate that exposure to high levels of VOCs can cause diseases in humans. In addition, due to the presence of toxic and heavy metals, as well as a minor proportion of organic solvent compounds (such as dissolved organic carbon), paint sludge may be classified as hazardous waste [16,17]. According to the available reports and studies, exposure to high concentrations of VOCs, whether accidental or short-term, can lead to irritation of the eyes, nose, throat, and lungs, as well as potential damage to the liver, kidneys, and central nervous system. Additionally, prolonged exposure to even low levels of VOC concentration could result in various health issues such as asthma, reduced pulmonary function, cardiovascular disease, and an increased risk of certain types of cancer [18–20]. According to EU Legislation, landfilling of water-based paint sludge is not permitted due to its high dissolved organic carbon content [6].

As previously mentioned, the high dissolved organic carbon (DOC) content of paint sludge makes it unsuitable for landfilling. However, this feature could be advantageous for biogas generation and compost production, making paint sludge a valuable source of biogas production [16]. Anaerobic digestion is a cost-effective method for managing paint sludge, as it reduces organic contaminant discharge into the environment while producing biogas. Biogas production through anaerobic waste digestion could be considered a source of renewable energy for CO_2 reduction and fossil fuel replacement strategies in the future.

Electrically conductive carbonaceous materials such as biochar and granular activated carbon play a crucial role in improving methane generation compared to other supplements [21,22]. Biochar, in particular, has unique physicochemical properties that result from factors such as pyrolysis operating status, activation process, and feedstock control, giving it an advantage over other supplements. Additionally, biochar is significantly cheaper than activated carbon, and any remaining biochar can be repurposed to enhance soil characteristics [23,24]. Biochar has proven to be beneficial in anaerobic digestion processes, as it enhances performance and helps maintain equilibrium in hydrolysis, acidogenesis-acetogenesis, and methanogenesis stages. It also plays a role in mitigating the effects of inhibitors. Biochar serves as a support for microbial colonies and strengthens buffer capacity, thereby promoting the biomethane production process. It establishes a robust chain of electron transfer between fermentative bacteria and methanogens. Investigating the roles of biochar in acid-buffering, propionic acid removal, and enhancing syntrophy between hydrolysis and acidogenesis-acetogenesis is suggested as a key area for future research [24–26]. Additionally, biochar's highly porous structure provides a larger surface area for CO_2 removal, further enhancing its effectiveness [27]. It can also improve the process stability, accelerate the process rate, buffer potency and alkalinity, inhibitors adsorption, enriched microbial functionality, electron transfer mechanism, reduce the lag phase, increase methane yield, and lower inhibitors in the anaerobic digestion process [24,28].

The objective of this study was to propose an effective method for treating automotive paint sludge through combination of the anaerobic method and the addition of biochar for recycling (in order to not only decrease the hazard of this waste but also produce biogas). Additionally, it aims to compare the impact of two different biochar doses on the performance of automotive paint sludge anaerobic digestion under mesophilic conditions at a laboratory scale. The results of this research will be useful for optimizing the treatment process for paint sludge, and for identifying the optimal dose of biochar for maximum efficiency.

2. Materials and methods

2.1. Substrate and inoculum sources

The water-based paint sludge sample for mesophilic anaerobic digestion experiments was collected from an Iranian automobile factory's paint shop for this study. The anaerobic sludge (inoculum) sample was collected from an anaerobic digester of a waste-water treatment plant located in Tehran. The substrate and inoculum were sealed and refrigerated at 4 °C.

2.2. Biochar production

The primary raw material used to produce biochar in the study is wood. According to scientific literature, biochar made from

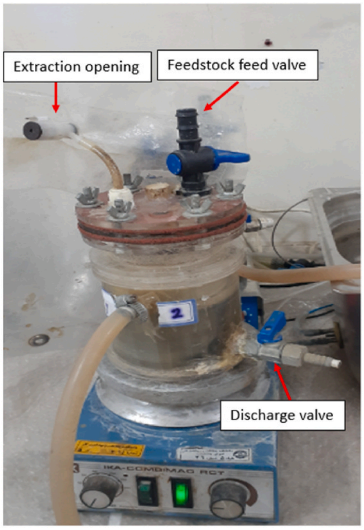

Fig. 1. Anaerobic digestion reactor.

conifers has better properties [29], so pine wood was used to prepare the biochar. The wood is cut into rectangular cube pieces with the dimensions of 10 l × 3 W × 2 H cm in order to fit the dimensions of the pyrolysis device (furnace) which was 11 l × 4 W × 3 H cm. Pyrolysis temperature is a significant parameter that influences the physicochemical properties of biochar, and some researchers reported that pyrolysis performed at 350–600 °C is more efficient for biochar production in terms of stability [30]. The pine wood was pyrolyzed at 600 °C for 2 h at a heating rate of 10 °C/min. Then the biochar is smashed and separated by particle size using 40 mesh sifters.

In order to measure the pH of biochar, a suspension was made by adding 5 g of biochar to 100 ml of distillate water and stirred for a complete day at 160 rpm [30]. The Brunauer-Emmett-Teller (BET) technique has been used to analyze the biochar's specific surface area. Main characteristics of produced biochar are presented in Table 1.

2.3. Experimental design

The mesophilic anaerobic digestion process was carried out using a multi-part system (which consists of anaerobic digestion reactor, Ben Marie, gas collection bag, magnetic shaker, etc.) in this study. A 500 ml total volume (and 200 ml working volume) anaerobic digestion reactor is made of a double-walled plexiglass bottle (Fig. 1). A discharge valve is located in the lower part of the reactor, and a feedstock feed valve is located on top of the reactor. Furthermore, an extraction opening for the produced gas is placed on the reactor's top, and the gas collection bag is connected to this opening.

In order to create an optimal temperature environment for the mesophilic system, Ben Marie was employed in this study to deliver and circulate water at the desired temperature (specifically 37 °C in this particular experiment) to the outer wall of the reactor. To prevent the accumulation of hydrogen partial pressure, 20% (100 ml) of the reactor space was left empty. The entire reactor was effectively sealed using glue to ensure airtight conditions. Also, to achieve an anaerobic environment, nitrogen gas was introduced into the reactor for a duration of 15 min. This step effectively displaced the oxygen present in the system, creating an oxygen-free environment necessary for the intended anaerobic conditions. And finally, a Tedlar bag was connected to the extraction opening of the digester in order to collect and store the produced gases (Fig. 1).

Some physicochemical parameters of paint sludge and inoculum (anaerobic sludge) were measured at the beginning of the experiment including VS (based on APHA 2540 E [31]), TS (based on section 2540 G of APHA standard method [31]), COD (based on section 5220 D of APHA standard method [31]), pH (based on EPA 9045 D [32]), alkalinity (based on APHA 2320; for automotive paint sludge, inoculum, and the combination of these sludges). Furthermore, some additional parameters including FS (based on APHA 2540 E), BOD (based on APHA 5210 B), P (based on APHA 4500 P), Organic C (based on Walkley-Black method), and N (based on Kjeldahl method) were measured for the paint sludge sample and the combination of inoculum and automotive paint sludge.

In addition, the physical and chemical properties of the resulting sludge (combination of inoculum and automotive paint sludge) were measured after combining inoculum and paint sludge at a 1:3 ratio (mixture of 50 ml of anaerobic sludge and 150 ml of automotive paint sludge). As the main substrate has an approximate amount of 40% water in it, in order to prepare the smooth feed stock, after combination with the inoculum, it should be stirred. The total solids and volatile solids parameters were measured before and after the incubation process. Biochar was added to an anaerobic digestion reactor at two specific doses of 10 g/l and 26 g/l, and a control sample was also included without biochar [30]. The impact of the varying biochar doses was then evaluated by measuring biogas production over a period of one month. The experimental setup consisted of three samples based on previous research sewage sludge [30]: the control sample without biochar, the second sample with a 10 g/l biochar dose, and the third sample with a 26 g/l biochar dose.

Table 2
The physicochemical properties of the paint sludge obtained from an automotive manufacturer.

Parameter	Unit	Value	Standard
pH	–	8.2	EPA 9045 D
TS	%	65	APHA 2540 G
VS	%	79	APHA 2540 E
FS	%	20.95	APHA 2540 E
BOD	mg/l	11,250	APHA 5210 B
COD	mg/l	16,584	APHA 5220 D
BOD/COD	–	0.6	–
P	mg/l	0.15	APHA 4500 P
Organic C	%	14.6	Walkley-Black
N	%	0.49	Kjeldahl
Alkalinity	mg/l $CaCO_3$	3400	APHA 2320
C:N:P	–	97.3 : 3.26 : 1	–

Table 3
The physicochemical characteristics of anaerobic sludge obtained from WWTP in south of Tehran.

Parameter	Unit	Value
pH	–	7.4
TS	%	1.8
VS	%	70
COD	mg/l	10,000
Alkalinity	mg/l $CaCO_3$	4500

Each sample was subjected to two replications of the experiment. The samples were placed in 200 ml reactors and sealed with appropriate covers to maintain anaerobic conditions. To achieve anaerobic conditions, the air in the headspace of the reactors was replaced with purged nitrogen gas for 10 min. The reactors were then incubated at 37 °C and stirred with a magnetic shaker (at 70 rpm) to prevent sedimentation. In this study, the gas volume generated was determined using the water displacement method at regular weekly intervals. This method assumes that the volume of the gas produced is equivalent to the volume of water expelled in the water collector. To facilitate this measurement, each digester was connected to water chambers, which were plastic bottles, through a plastic pipe called the gas pipe. This gas pipe allowed the produced gas to flow into the water chamber. Another plastic pipe, known as the water pipe, was used to transfer the displaced water from the water chamber to the water collector, which was tightly sealed with an M-seal. Both ends of the gas pipe were positioned at the uppermost part of the digester and water chamber to ensure accurate measurement. Meanwhile, the water pipe was submerged in the water chamber and positioned at the top of the water collector [33]. In addition, gas chromatography was employed to analyze a representative sample of the biogas for its volume and the removal of chemical oxygen demand (COD). The gas chromatography was conducted using a thermal conductivity detector (TCD) with a 1 ml sample injection volume and hydrogen as the carrier gas, under the following conditions: i) a temperature increase rate of 10 °C per minute and ii) a column temperature of 40 °C, an injector temperature of 100 °C, and a detector temperature of 150 °C [34].

3. Results and discussion

3.1. Paint sludge analysis

For this study, water-based paint sludge was collected from the paint booth and transported to the laboratory for analysis. Standard methods were used to determine the physicochemical properties of the paint sludge, and the resulting data are presented in Table 2.

According to Table 2, the pH value of automotive paint sludge in this study was around 8.2 which was within the range reported in previous studies (7.2–9.4) [7–9,35], indicating the alkaline properties of the sludge. As the water-based paint sludge contains some organic solvents (e.g., 2-butoxyethanol, Polyurethane, Naphtha, etc. [6]), it has a high BOD/COD ratio (as it is reported in Ref. [36]) which makes it a suitable substance for anaerobic digestion process.

There are direct inhibitors such as heavy metals and organic compounds; and indirect inhibitors, such as volatile fatty acids (VFAs), hydrogen, ammonium and sulphides in anaerobic digestion process [37]. One of the benefits of using biochar in anaerobic digestion process is reducing the presence of inhibitors [38]. Moreover, the potential for biochar addition to increase methane yield has been reported in various literature, through a range of mechanisms including: (a) enhancing the buffering capacity of the anaerobic digestion process, (b) immobilizing microbial cells, (c) enhancing syntrophic metabolisms, (d) improving digestion quality, (e) promoting and cleaning biogas, and (f) reinforcing direct inter-species electron transfer (DIET) [38,39].

The inoculum was obtained from the anaerobic digester sludge at South Tehran's wastewater treatment plant (WWTP). The sludge's physicochemical properties are displayed in Table 3.

After mixing automotive paint sludge and anaerobic sludge at a 3:1 ratio (150 ml of automotive paint sludge and 50 ml of anaerobic sludge), the physical and chemical properties of the resulting sludge were measured and presented in Table 4.

Table 4
The physicochemical properties of the combined paint sludge and anaerobic sludge.

Parameter	Unit	Value
pH	–	8
TS	%	60
VS	%	75
FS	%	24.27
BOD	mg/l	9928
COD	mg/l	15,600
BOD/COD	–	0.6
Organic C	%	12.1
N	%	0.59
Alkalinity	mg/l $CaCO_3$	3700
C/N	–	20.51

The presence of organic matter in combined paint sludge and anaerobic sludge could be revealed by the BOD and COD of 9928 mg/l and 15,600, respectively. For a biodegradable feedstock, the potential for biogas production highly depends on the C/N ratio. From Table 4, approximately, the C/N ratio of 20:1 was obtained which reveals that combined sludge has a good potential for biogas production.

3.2. Modification of pH during anaerobic digestion process

The pH of all samples was measured at the end of each week, with sample 1 exhibiting pH values of 8.1, 7.8, 7.6, and 7.6 after the first, second, third, and fourth weeks of anaerobic digestion, respectively. Sample 2 had pH values of 8.1, 7.6, 7.2, and 7.4, while sample 3 exhibited pH values of 8.1, 7.5, 7.4, and 7.2 over the same time period. Overall, the pH of all samples demonstrated variability within the range of 7.2–8.1. In the anaerobic digestion process, the activity of methanogens may be impacted by variations in pH. Methane-producing bacteria exhibit greater activity under neutral pH conditions, while pH fluctuations above or below this range may constrain the activity of methanogens [40]. In the context of anaerobic digestion, biochar plays a significant role in electron donation and acceptance, which can be considered as a method to regulate pH levels during the process and promote biogas production under neutral pH conditions. Specifically, in anaerobic digestion, the rapid accumulation of volatile fatty acids (VFAs) leads to a low-pH environment. At this stage, certain functional groups present in biochar, such as amine groups, adsorb H+ ions and accept electrons, thereby mitigating the sudden pH drop. Moreover, the ash component of biochar contains various inorganic materials (like Ca, K, Mg, Na, Al, Fe, Si and S). Among these, alkali and alkaline earth metals are responsible for the alkalinity of biochar. These inorganic components contribute to the overall buffering capacity of biochar, aiding in maintaining a stable pH environment during anaerobic digestion.

During the first week of the anaerobic digestion process, acid-forming bacteria demonstrate heightened activity, primarily generating organic acids that facilitate the breakdown of organic matter within the feedstock. Acidification is a crucial process in which VFAs are generated as substrates for methane production by methanogens. Acidogenic fermentation bacteria convert soluble monomers into short-chain fatty acids, such as acetic acid and propionic acid, which are the end products of this process. Acetic acid serves as a direct substrate for methanogens, playing a vital role in methane production. There are two pathways for VFA production. Firstly, simple organic wastes like monosaccharides and proteins are taken up by acetogens, resulting in the production of short-chain acids (acetic acid, propionic acid, butyric acid, etc.). Secondly, a small portion of acetogens, such as homoacetogenic bacteria, can utilize carbon dioxide and hydrogen as substrates, converting them into acetic acid. Hence, promoting either pathway enhances the rate of acidification. Acetic acid, being a major intermediate product, significantly influences methanogenesis. Complex organic matter can be hydrolyzed into various types of mono substrates, some of which are easily degradable while others are not. Consequently, the bioconversion of difficult-to-degrade substrates into acetic acid and hydrogen, which are important intermediate products, has a significant impact on increasing methane generation [28]. This process subsequently enhances the overall acidity of the anaerobic digestion system. Notably, the third sample exhibited a more significant difference between initial and final pH values than the other samples, likely due to the pH levels nearing neutrality during the last three weeks of the anaerobic digestion process, which created more suitable conditions for methanogens to thrive.

In an anaerobic digestion process, from the additive point of view, biochar can donate and accept electrons [41]. Furthermore, biochar's buffer capacity is mainly depended on two factors: (I) Functional groups: during anaerobic digestion process, fast accumulation of VFAs causes a medium with low pH amount in which some biochar's functional groups (such as amine) adsorbs H^+ and accepts electron. This phenomenon could alleviate the abrupt pH drop; (II) Inorganic materials: Ash portion of biochar includes inorganic materials (like Ca, K, Mg, Na, Al, Fe, Si and S). Among them, alkali and alkaline earth metals are responsible for alkalinity of biochar [42].

Linville et al. (2017) investigated the influence of biochar from walnut shell during the anaerobic digestion and reported that biochar increased the stability of process by improving the total alkalinity and pH [43]. Regarding the abovementioned point, in this study, the modification of pH in presence of biochar might be a result of rapid break down.

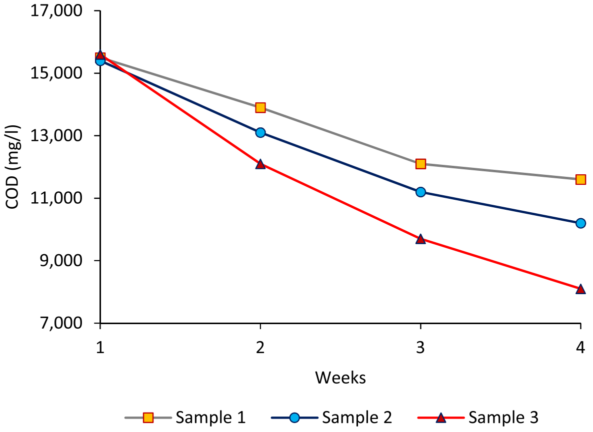

Fig. 2. COD variations for the first (the control sample without the presence of biochar), the second (with addition of 10 g/l), and the third sample (with addition of 26 g/l).

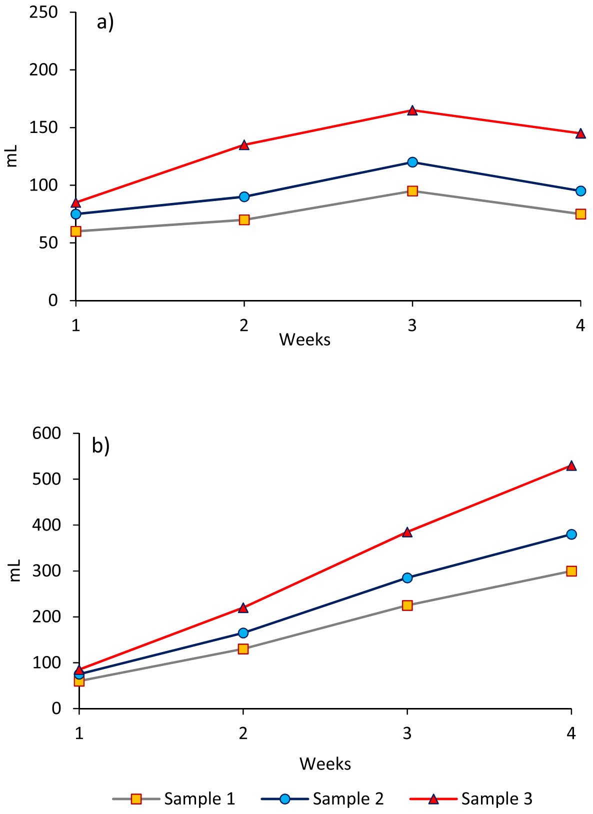

Fig. 3. a) the weekly and b) cumulative volume of produced biogas (mL) for the first (the control sample without the presence of biochar), the second (with addition of 10 g/l), and the third sample (with addition of 26 g/l).

3.3. Variation of COD during anaerobic digestion process

Microorganisms play a crucial role in breaking down organic materials during anaerobic digestion, resulting in their conversion to simpler compounds and a subsequent decrease in their concentrations. This process not only reduces the organic pollution present in wastewater but also generates biogas as a by-product [44–48]. The reduction in COD during anaerobic digestion serves as a metric for the extent of organic material breakdown. As demonstrated in Fig. 2, biochar addition leads to a more substantial decrease in COD levels. Specifically, the introduction of biochar to the mesophilic anaerobic digestion reactor produces a further reduction in COD (compared to its initial value), resulting in reductions of 25, 33, and 48% for the first, second, and third samples, respectively.

For the COD, the lag period in the first stage reveals the commencement of the feed stock decomposition which resulted in a little difference between the initial COD with the measured COD at the end of the first week (both were around 15,600 mg/l). At this stage micro-organisms' function is not very significant. The second stage, which is from the onset of the second week till the end of the third week, is a stage of substantial COD reduction which reveals a period of more quick biological degradation of the substrate's organic content. The final stage, which is from the initiation of the fourth week till the end of this week, is a stage of another gradual or less quick COD reduction. Before this final stage, greater amount of the feed stock's organic content has been decomposed which results in existence of less organic content in the reactor.

Wambugu et al. (2019) reported that the COD removal efficiency was higher in the reactor with the biochar amendment than in control reactor [49]. Ejimofor et al. (2021) reported that the highest level of COD reduction in the anaerobic digestion of paint wastewater was achieved during the third week (around 45%), with a subsequent gradual decrease in COD levels [50]. Similarly, the findings of the present study demonstrate that the most significant reduction in COD levels occurred by the end of the third week of the anaerobic digestion process with the removal efficiency of 48%.

3.4. Variation of VS during anaerobic digestion process

The initial and final volatile solids (VS) content of all samples were measured in the current study. The results indicate that the addition of biochar led to a decrease in the VS content of the samples, resulting in final values of 54, 48, and 32% for samples 1, 2, and 3, respectively. These final values were lower than the initial VS content of 75% for all samples, suggesting that biochar may have a significant impact on reducing VS levels. Previous studies have reported significant reductions in VS during anaerobic digestion [38,51,52]; for example, Capela et al. (2008) reported 40–50% VS removal during anerobic digestion for different raw materials (including industrial sludge and cattle manure. As VS is a crucial factor in determining the feedstock's biodegradability potential, a higher reduction in VS implies a greater potential for biodegradability and biogas production. The observed VS reduction of 43% (from an initial value of 75% to a final value of 32%) for the third sample indicates a high level of biodegradability potential and potential for biogas production.

3.5. Biogas production

This study also investigated the impact of incorporating biochar on the volume of biogas generated through the anaerobic digestion of automotive paint sludge. Fig. 3a and b present the weekly and cumulative biogas production of the first, second, and third samples.

The biogas produced from sample 1 was 60, 70, 95, and 75 ml in the first, second, third, and fourth weeks, respectively, resulting in a cumulative biogas production of 300 ml (Fig. 3a). The biogas production results for sample 2 were 75, 90, 120, and 95 ml, with a cumulative production of 300 ml (Fig. 3b). For sample 3, the values were 85, 135, 165, and 380 ml, with a cumulative production of 530 ml. The maximum biogas production in this study was observed at the third week of the anaerobic digestion process, as indicated by the measurements. The findings show that the addition of biochar had a substantial impact on increasing the volume of biogas produced.

In order to compare the effect of biochar on the biogas production from anaerobic digestion of the mixture of industrial sludge (paint sludge) and sewage sludge, in the study of Zhang (2019), it is reported that compared with the blank group, the cumulative biogas yield increased by 28 and 57% when the amount of biochar added was 10 and 26 g/l, respectively [30]; however, in our study, biochar supplementation enhanced the biogas production volumes, with the 27 and 76% when the amount of biochar added was 10 and 26 g/l, respectively.

A comparison between produced biogas and reduced VS in this work with the work of Ejimofor et al. (2021) shows that the VS final values of the samples in the present study was 54%, 48%, and 32% for samples 1, 2, and 3, respectively; which resulted in cumulative biogas generation of 300, 380, and 530 ml, respectively; while Ejimofor et al. (2021) used a mixture of 150 g of post coagulated sludge of paint wastewater and 450 ml of water (in a 1 l sealed gallon, with 750 ml working volume), and finally, the VS value of the sample was 62.3% which resulted in 220 ml biogas production [50].

In order to compare the produced biogas and COD reduction in this work with the work of Bajaj and Winter (2013), using high strength automobile industry wastewater, they reported a COD reduction of 20% (from 10,000 to 8000 mg/l) during anaerobic digestion process which resulted in 100 ml biogas production (0.05 ml/(mg/l reduced COD)) [1]; while in the present study, 48% COD reduction (from 15,600 to 8100 mg/l) in the third sample resulted in 530 ml biogas production (0.07 ml/(mg/l reduced COD)).

The findings of this study align with those of Ejimofor et al. (2020) and Ejimofor et al. (2021), who reported that the maximum biogas production during anaerobic digestion of paint wastewater occurred in the third week, after which the biogas production decreased [36,50].

Wang et al. (2018) reported that with the addition of biochar (4 g/l), the lag time of methanogenesis was shortened by 28.6% (as the direct transfer of electron through a fixed path could facilitate the stable methanogenesis), the strengthening factor of COD removal rate reached 1.6 (to provide a new strategy for developing high-rate anaerobic digestion system), and the electric conductivity of sludge reached up to 2-fold amount (which shows that the electron transfer characteristics of sludge improved obviously). According to their results, the biochar addition simplifies the selective enrichment of potential DIET partners (like Methanothrix and Geobacter species) for improving the DIET process [53].

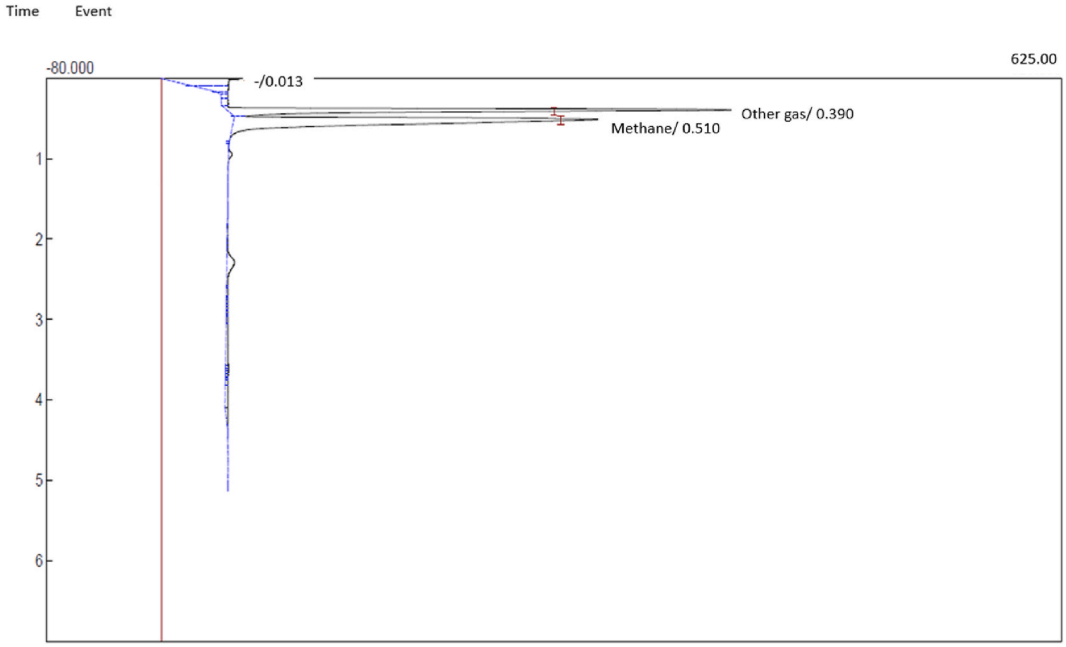

Fig. 4. The gas chromatography results of the biogas obtained from the third sample (at the end of the fourth week of anaerobic digestion process).

3.6. Confirmatory gas chromatography test

The gas chromatography results for the biogas from the third sample, taken at the end of the fourth week, are displayed in Fig. 4. The results indicate that methane made up approximately 50% of the produced biogas. In a previous study by Ejimofor et al. (2021), the produced biogas was found to contain approximately 63% methane, which is comparable to the amount reported in the current study [50]. It should be noted that the different methane yield in these two studies could be due to the use of different substrates and inoculums (paint wastewater versus paint sludge). Nevertheless, the high percentage of methane in the biogas classifies it as relatively high-quality, which is promising for potential energy applications [54].

4. Conclusion

The primary objective of this study is to investigate the impact of biochar supplementation on biogas production volume during the one-month mesophilic anaerobic digestion process of automotive paint sludge. To achieve this goal, the experiment considered three samples, including two biochar-dosed samples at different concentrations (10 and 26 g/l), and a control sample without biochar addition. The findings indicate that biochar addition to the mesophilic anaerobic digestion reactor results in a further reduction of COD compared to the initial levels, with incremental biochar additions leading to 25, 33, and 48% reductions in COD for the first, second, and third samples, respectively. Additionally, the addition of biochar leads to a reduction in VS during the digestion of organic matter, with a greater reduction observed in samples with higher biochar concentrations (21, 27, and 43% for the first, second, and third samples, respectively), indicating the beneficial effect of biochar. Moreover, biochar supplementation enhances both weekly and cumulative biogas production volumes, with the third sample producing the highest cumulative volume of biogas (530 ml) compared to the control (300 ml) and the second sample (380 ml). Finally, gas chromatography analysis of the biogas from the third sample revealed that approximately 50% of the produced gas is methane. An inverse relationship between the cumulative biogas production volume and COD levels was observed.

Author contribution statement

Nadali Alavi: conceived and designed the experiments, contributed reagents, materials, analysis tools or data.

Mohsen Sadani: conceived and designed the experiments; analyzed and interpreted the data.

Abbas Shahsavani: conceived and designed the experiments; performed the experiments.

Reza Bakhshoodeh: contributed reagents, materials, analysis tools or data; analyzed and interpreted the data; wrote the paper.

Marzieh Moradi: performed the experiments, wrote the paper, analyzed and interpreted the data, contributed reagents, materials, analysis tools or data.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Reza Bakhshoodeh reports financial support was provided by the Shahid Beheshti University of Medical Sciences for their financial support (No. 31525).

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