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Experimental evaluation on the effect of biochar addition with anaerobic digestion of the tannery wastewater to improve biogas production

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ABSTRACT

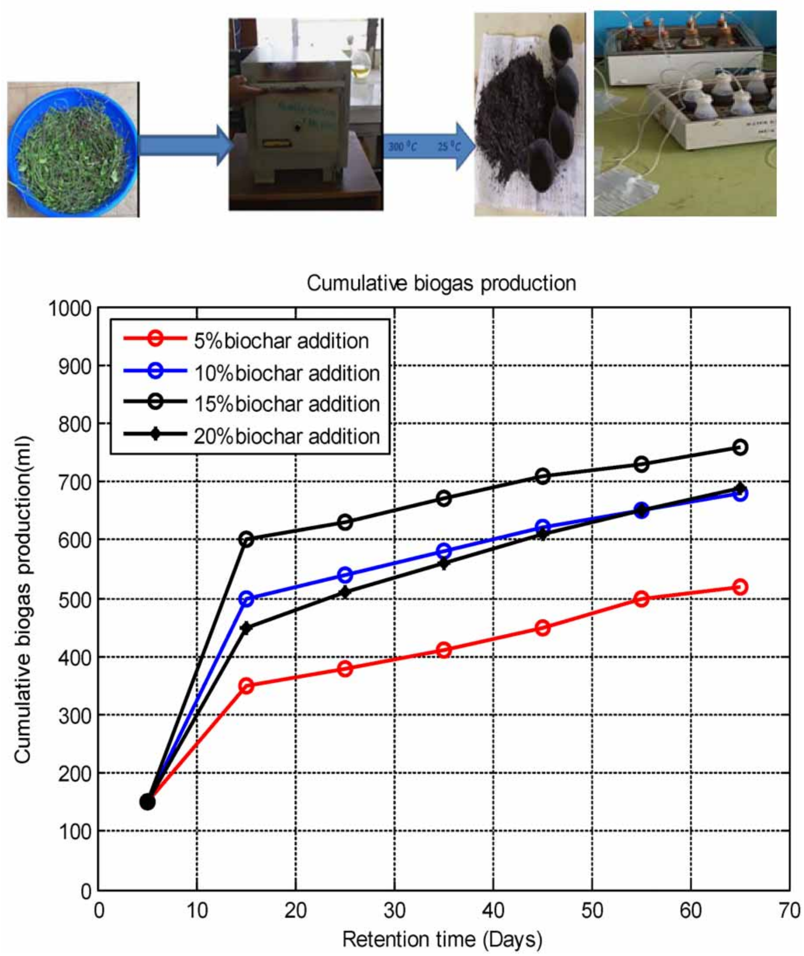
The use of biochar as an additive material in various compositions to the anaerobic digestion of the tannery wastewater was investigated. Pyrolytic biochar made from Khat waste with different compositions was added to anaerobic batch digesters in laboratory-scale experiments. Biogas digesters of 500 ml volume were used to explore the effects of biochar on anaerobic digestion in the ratios of 5, 10, 15, and 20% (w/w) at constant mesophilic temperature (38 °C). The results show that for five experimental tests in digesters (D0, D1, D2, D3, and D4), which contains 0, 5, 10, 15, and 20% of biochar, the cumulative methane and biogas yields were, respectively, 17.04, 41.2, 43.8, 51.6, 48.6% and 150, 520, 680, 760, 690ml. Compared to the cumulative methane production efficiency of the digester without biochar (D0), the addition of 5, 10, 15, and 20% biochar had more favorable effects and increased the efficiency by 58.6, 61.1, 66.98, and 64.94%, respectively. From these results, adding 15% of biochar to anaerobic digestion causes a three-fold increase in methane compared to the control and more positive effects than all other biochar compositions. According to this result, the right dose of biochar must be added to maximize biogas production.

Key words: biochar, biogas, anaerobic digestion, Khat (*Catha edulis*) waste, tannery wastewater

HIGHLIGHTS

- Biochar addition in the right dose can increase methane yield from anaerobic digestion.
- Tannery waste water treatment requires an inexpensive route to remove contaminants.
- Biogas quality and quantity are enhanced by adding biochar to tannery waste water.

GRAPHICAL ABSTRACT



NOMENCLATURE

AAiT	Addis Ababa Institute of Technology
AD	anaerobic digestion
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
BC	biochar
BOD	biochemical oxygen demand
COD	chemical oxygen demand
OC	organic carbon
TN	total nitrogen
TS	total solids
TWW	tannery wastewater
VS	volatile solids

1. INTRODUCTION

Energy plays a critical role in the production of commerce and industry (Ajcharap *et al.* 2019) to meet our basic needs. As the global population rapidly increases, energy demand and its impact on global climate and ecosystems also tend to increase. In the majority of developing nations, continuing use of fossil fuels results in greenhouse gas emissions, which have a negative impact on both human health and the environment (Junluthin *et al.* 2021). Since the linear economy based on fossil fuels has so many serious problems, we need to embrace a bio-economy that produces more environmentally friendly energy sources (Gotore *et al.* 2021).

Renewable energy is environmentally friendly energy produced from sources like biomass, geothermal resources, sunlight, water, and wind that are naturally replenished and can be converted into clean energy and as such promote carbon neutrality. The majority of studies in this regard have come to the conclusion that 100% renewable energy is practicable and affordable everywhere (Breyer *et al.* 2022).

Biomass is a renewable resource that has been considered an alternative feedstock to provide sustainable and clean energy. Previous studies have demonstrated that it is possible to generate a wide variety of bioenergy from biomass residues and wastes (Lee *et al.* 2019). Waste-to-energy conversion reduces greenhouse gas emissions in two ways. When heat and electrical energy are generated from waste, the reliance on fossil fuels is reduced while the greenhouse gas emissions are considerably decreased by avoiding methane emissions from landfills (Wannapokin *et al.* 2018).

Wastes are generated from different production activities including agricultural wastes, industrial waste, commercial waste, and construction waste. Tannery waste is one of the most highly polluting and the worst possible solid and liquid industrial wastes generated from leather factories. Around 700 kg of sludge and 30–35 m^3 of effluent containing 400 kg of suspended and dissolved particles with high chemical oxygen demand (COD), chromium, sulfide, and other organic as well as inorganic pollutants are released for every 150 kg of the final leather product (Pal *et al.* 2020). The chemicals employed in various phases of the leather tanning process, such as sulfides, sulfates, chlorides, tannins, and heavy metals, are the main cause of pollution in tannery wastes. Since tannery effluents are very toxic and have an adverse effect on agricultural lands and water sources, utilizing these industrial wastes to generate renewable energy, reduce environmental pollution, and provide sustainable solutions to the energy demand problem is a way forward (Teklay *et al.* 2018).

Ethiopia, a country in eastern Africa, has a large cattle resource that may provide plenty of raw materials for the manufacturing of footwear, clothing, and other commodities (Teklay *et al.* 2018). Currently, there are more than 30 tanneries operating in Ethiopia, which generate 11,312 m^3 of wastewater every day, more than 70,104 tons of solid waste, and 412,888 m^3 of wastewater every year, all of which are dumped into the environment without proper treatment (Mekonnen *et al.* 2017). The Modjo Tannery Share Company, which operates in Modjo Town, Ethiopia, generates 2,460 tons of solid waste, and 122,700 m^3 of untreated wastewater annually and is disposed of into the surrounding without proper treatment. Such large amounts of leather waste create a serious effect on aquatic biota, soil pollution, air pollution, and safety aspects which consequently create a health risk (Berhe 2017).

To make these wastes environmentally friendly and economically viable, there should be a conversion mechanism which turns these wastes into renewable energy. The waste-to-energy conversion technologies such as incineration, anaerobic digestion (AD), pyrolysis, and gasification were employed to convert different wastes to useful energy. Based on the sustainability evaluations of waste-to-energy generation systems in terms of economy, environment, and social aspects, AD is found as the most sustainable waste-to-energy technology (Khan & Kabir 2020).

AD is a method used for producing biogas from the biological degradation of solid and liquid waste. It is a promising means of addressing global energy needs and providing multiple environmental benefits through converting industrial wastes into biogas (Yuwalee *et al.* 2019). In contrast to other renewable energy sources like wind or solar power, biogas is produced irrespective of weather conditions and can be stored, making it available whenever needed. Biogas is a basic source of renewable methane produced from the AD of biomass in the absence of oxygen. The process is carried out in digesters under a series of metabolic interactions (hydrolytic, acidogenic, acetogenic, and methanogenic) among various groups of microorganisms (Agustini *et al.* 2018).

The production of biogas is influenced by the types of substrates used and operational parameters such as pH, temperature, organic loading rate, and retention time. The characteristics of the substrate used as a feedstock for biogas production inhibit the performances of AD. According to previous research reported, substrate-induced inhibition is a major issue, which can disrupt the stable functioning of the AD system reducing microbial breakdown of the organic waste and formation of methane, which in turn reduces biogas production (Breyer *et al.* 2022). The challenges in AD of tannery wastewater (TWW) are its high levels of chemicals such as lime, sodium carbonate, sodium bicarbonate, common salt, sodium sulfate, chrome sulfate, fat liquors, vegetable oils, dyes, and other compounds generated during leather processing which inhibits the metabolic activities of microorganism participating in AD process (Achouri *et al.* 2017). In addition to the chemicals used in the leather-making process, TWW has an unfavorable carbon-to-nitrogen ratio that frequently leads to the generation of ammonia, which inhibits the biological activities of microorganisms responsible for biogas production. Therefore, in its raw form, TWW is not a suitable substrate for AD (Manyuchi 2018).

Biochar could be directly added to the AD reactor to stabilize the process as well as to improve the methane production efficiency. The merits of biochar addition in AD were reported to be the adsorption of organic compounds or heavy metals, the increase of buffering potential, the potential of direct electron transfer, to act as the microbial carriers to increase the microbial concentration and facilitate metabolic activities of microorganisms responsible for biogas production (Ma *et al.* 2020).

Different studies have shown the AD of TWW along with various types of bio-wastes. However, there are no studies reported yet on the effects of biochar addition to the AD of TWW. The goal of this study was to investigate how addition of different amounts of biochar to the AD of TWW can improve the stability of AD and enhance biogas yields under fixed mesophilic temperature (38 °C).

2. MATERIALS AND METHODS

2.1. Materials and chemicals

The materials used in this study were as follows: evaporating dish, water bath, oven, desiccators, analytical balance, dish tongs, filters, crucible, crucible tongs, biogas analyzer, plastic bottle digesters, furnace, thermogravimetric analyzer, gas syringe, geotech, bomb calorimeter (TESTMASTER), pH-meter, and thermometer. The chemicals used were $NaHCO_3$, HCl, and NaOH.

2.2. Sample description

The TWW sample was collected from Modjo Tannery share company that is situated in Modjo town located 80 km south of Addis Ababa in Ethiopia and at a latitude and longitude of 8°35′ N and 39°07′E, respectively, with an elevation between 1,788 and 1,825 meters above sea level. The TWW samples were poured into the bottles and stored in an icebox and transported to Addis Ababa University Institute of Technology (AAiT), School of Bio and Chemical Engineering, and kept refrigerated until further analysis.

The second sample used in this study was Khat waste for biochar production. The Khat waste was collected from a different place in Jimma town and its characterization was conducted at Jimma University College of Agriculture and Veterinary Medicine, Ethiopia, which is located 350 km southwest of Addis Ababa.

2.3. Experimental design and setup

The TWW digestion experiments were conducted in five different mixing ratios of TWW and biochar. The mixing ratios used were (100%:0%), (95%:5%), (90%:10%), (85%:15%), and (80%:20%) of TWW to biochar by weight. All five digesters' bottles were fed with TWW once in every 10 days. The biogas content was periodically measured using a biogas meter. The reactors were operated at a temperature of 38 °C.

2.4. Experimental setup

Bench-scale anaerobic digesters were prepared using 500-ml glass bottles. The bottles were sealed with rubber stoppers to maintain anaerobic conditions. The rubber stopper has connection with two hose gas pipes each with 8 mm internal diameter and 1 m length. One of the hose gas pipes was used to feed TWW and discharge the treated supernatants after 10 days. The other hose gas pipe was used to collect the biogas produced during AD. At the top of the second hose, a plastic bag was used to collect the biogas and it has two valves; they were closed only during the period of measurement of the biogas which was produced during operation. The temperature of the digester was maintained at 38 °C using water baths. Figure 1 shows an experimental setup.

2.5. Characterization of TWW

In this study, the physicochemical properties of TWW were determined before AD. The physicochemical properties of feedstock (TWW) include the determination of total solids (TS), volatile solids (VS), total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), alkalinity, pH, the carbon-to-nitrogen ratio (C/N), free ammonia and ammonium using the American Society for Testing and Materials (ASTM) standard.

Figure 1 | Experimental setup of digesters.

2.5.1. Determination of total solid contents

TS are the residue that remains after evaporating a known volume of sample and then drying it in an oven at a specific temperature. TS include total suspected solids and TDS. The weight of the sample and the weight of the dish were recorded. The sample was placed into a convection oven at 105 ± 3 °C for a minimum of 4 h. The sample was removed from the oven and cooled to room temperature in a desiccator. The dish containing the oven-dried sample was weighed to the nearest 0.1 mg. The sample was placed back into a convection oven at 105 ± 3 °C and dried to constant weight. Constant weight is defined as ±0.1% change in the weight percent solids upon 1 h of re-heating the sample. Overnight drying is usually required for very wet or liquid samples (Choi *et al.* 2020). The TS of TWW was calculated from Equation (1).

From this experiment, the TS of TWW was calculated by the following formula.

$$\%\mathrm{TS} = \left(\frac{W_1 - W_2}{W_3}\right) * 100 \tag{1}$$

where %TS refers to the percentage of total solid, W_1 refers to the weight of dry crucible plus sample as received, W_2 refers to the weight of dry crucible, and W_3 refers to the weight of sample as received.

2.5.2. Determination of VS

The term total VS refers to materials that were obtained after TWW filtration is dried and ignited. The percentage of volatile solid contents of TWW was calculated using the following Equation (2).

$$\%\mathrm{VS} = \left(\frac{W_1 - W_2}{W_3}\right) * 100 \tag{2}$$

%VS refers to the percentage volatile solid, W_1 refers to the weight of dried crucible plus dried residue, W_2 refers to the weight of crucible plus residue after ignition, W_3 refers to the weight of dried residue.

2.5.3. Determination of moisture content

To determine TWW moisture content (MC), 2 g of fresh materials that were obtained after TWW filtration was dried at 105 °C for 24 h in an oven and weighed again. The percentage of MC was calculated by Equation (3).

$$\%\mathrm{MC} = \left(\frac{W_i - W_d}{W_i}\right) \times 100 \tag{3}$$

MC refers to the moisture content of the TWW, W_i refers to the initial weight of fresh TWW after filtration in grams, W_d refers to the weight of dried material at 105 °C in g.

2.5.4. Determination of carbon-to-nitrogen ratio

Organic carbon (OC) was determined by the Walkley-Black method and total nitrogen (N) concentration was determined by the Kjeldahl method. Then carbon-to-nitrogen ratio was calculated.

2.5.5. Determination of BOD

The sample was placed in an airtight bottle and incubated for 5 days at a particular temperature. The BOD was computed from the difference between the initial and final concentrations of dissolved oxygen, which are measured before and after the sample has been incubated for 5 days at 20 °C.

2.5.6. Determination of COD

The two approaches for determining COD are known as open reflux and closed reflux. In this work, the closed reflux principle was applied to determine COD.

2.6. Biochar production processes (from Khat waste)

Khat waste was collected from Jimma City and taken to Jimma University College of Agriculture, Department of Animal sciences laboratory for biochar production and characterization. The moisture of Khat waste was calculated by taking 80.89 g of freshly collected Khat waste and weighed using a digital balance and then placed inside an electric hot air oven at 105 °C for 24 h. After 24 h, the sample was taken out of the oven and reweighted by digital mass balance and then the MC of the sample was calculated. After that 2 g of oven-dried Khat waste sample was heated in a muffle furnace at a temperature of 550 °C for 3 h and the sample was cooled to room temperature and weighed again by digital mass balance which is equal to ash weight and the volatile solid was calculated by subtracting ash weight from 100.

For biochar production, 800 g of dry Khat waste sample was crushed to approximately 10 mm size. Then the crushed Khat waste sample was stored in crucibles and heated at a temperature of 300 °C with a residence time of 3 h in a muffle furnace with a sealed chamber to prevent airflow inside. The heating process was started to until the target temperature (300 °C) was obtained. The sample was then cooled to room temperature before being used for the test as shown in Figure 2.

2.7. Data analysis

Each experiment was conducted in triplicate with the average results reported. The MATLAB software R2022 was used for error analysis ($P > 98.06$).

3. RESULTS AND DISCUSSION

3.1. Characterization of TWW and biochar

3.1.1. Characterization of TWW

The substrates used for the biogas production at the bench scale were TWW and biochar mixed at different ratios. The Modjo tannery can process up to 8,500 sheep and goat skins and 500 hides each day, turning them into finished leather for both the domestic and international markets. The industry uses 650 m^3 of water per day and discharges 400–450 m^3 of wastewater per day. Three waste streams from the tanning process are discharged in separate canals: general wastewater, wastewater

Figure 2 | Khat waste pyrolysis processes during biochar production.

containing chrome, and wastewater containing sulfide. In this work, a TWW sample was taken from a general wastewater canal. Approximately 500 ml of inoculum was taken from an operating biogas plant at AAiT, Addis Ababa University.

According to APHA 20E 4500 NB (Baird *et al.* 2017) guidelines, the characteristics of the TWW used as a feedstock for biogas production were determined using its TS, VS, total nitrogen (TN), and carbon contents. The physicochemical properties of Khat waste-derived biochar, TWW, and four different types of biochar added to TWW are presented in Table 1.

As it was indicated in the above table, the TWW had average moisture and TS contents of the substrate 92.84 and 7.16%, respectively. The recommended amount of TS of feedstock for biogas production was between 5 and 15% (Kulichkova *et al.* 2020). In this study, the average TS value for TWW was 7.16%. The average values of VS and ash content of TWW were 76.24 and 23.76%, respectively. The results of VS in the table above suggest that a significant portion of TWW is biodegradable and can act as a feedstock for the production of biogas because VS indicates the potential for further digestion.

In this study, the average values for OC% and TN% were 28.14 and 1.58, respectively. The balance of carbon and nitrogen in the feeding material has a big impact on methane yield and production rates. From this experiment, the C/N ratio was 17.81, which is not favorable for the growth of microorganisms responsible for biogas production. For efficient biogas production, the C/N ratio in the feedstocks should be maintained in the range of 20–30:1 (Choi *et al.* 2020). To maintain the ratio of C/N at 20–30:1, biochar derived from Khat waste was added to the reactors containing TWW to adjust the C/N ratio.

3.1.2. Biochar (Khat waste-derived) characterization

The physicochemical properties of Khat waste-derived biochar were determined using the ASTM protocol. The characteristics of biochar feedstock (Khat waste) used as an additive material for biogas production were determined using its TS, VS, TN, and carbon contents. The physicochemical properties of Khat waste-derived biochar are present in Table 2.

The total solid of the Khat waste sample was calculated by taking 80.89 g of sunlight-dried lot and then placed inside an electric hot air oven at 105 °C for 24 h. After 24 h in the oven, the sample was taken out of the oven and weighed again by a digital mass balance, equal to 76.23 g. The composition of solids content remaining after heating the sample at 105 °C to constant weight was equal to 94.24%. The MC, volatile solid, and ash contents of the raw Khat sample were 5.76, 93.2, and 6.8%, respectively. The biochar derived from Khat waste has almost similar moisture to previously reported studies (Afessa *et al.* 2022).

The volatile solid of the Khat waste was determined by taking 2 g of oven-dried Khat waste sample at a temperature of 105 °C for 24 h and then this sample was heated in a muffle furnace at a temperature of 550 °C for 30 min. Then this sample was cooled to room temperature and weighed again by digital mass balance which is equal to 0.1358 g as Ash weight. Then, the volatile matter was calculated to be equal to 93.2%. This result is somewhat greater than the results reported by (Gabriel *et al.* 2021; Afessa *et al.* 2022).

Table 1 | The physiochemical properties of tannery wastewater

Parameter	Tannery wastewater
Moisture content (%)	92.84
TS (%)	7.16
VS (%)	72.24
Ash (%)	23.76
OC (%)	28.14
TN (%)	1.58
C/N ratio	17.81
pH	8.38
BOD5 (mg/l)	4,375
COD (mg/l)	4,543.5
Sulfide (mg/l)	0.53
Chloride (mg/l)	15,223.1
EC (mS)	8.63

Table 2 | Physicochemical properties of biochar produced from Khat waste

Parameters	Khat-derived biochar
Moisture content (%)	5.76
TS (%)	94.24
VS (%)	93.20
Ash (%)	6.80
OC (%)	42.87
TN (%)	1.5
C/N ratio	31.8

The ash content of the Khat waste sample was determined after the muffle furnace was adjusted to the temperature of 550 ± 25 °C. To avoid pre-ignition, the crucible was placed over the flame until smoke appears using an ashing burner, and the crucible was cooled before placing it in the muffle furnace. Then the crucible was placed in the muffle furnace at 550 °C for 30 min. The crucible was carefully removed from the furnace directly into a desiccator and cooled for a specific amount of time, equal to the initial cooling time of the crucible. The weight of the crucible and ash to the nearest 0.1 mg was recorded. The calculated percentage composition of the Khat waste ash was 6.8%. This result is slightly greater than the ash contents of Khat waste of the previous researchers (Afessa *et al.* 2022) and lower than the ash content determined by Gabriel *et al.* (2021).

3.1.3. Characterization of the combination of biochar and TWW

The physicochemical properties of four different percentages of biochar added to TWW are presented in Table 3.

The averaged values of TS, VS, and C/N ratio of four different percentages of biochar added to TWW are presented in Table 3. For biochar added to TWW, the TS obtained in this study are in the range of (8.48–12.44%), which is greater than the total solid contents of TWW results reported by (Andualem *et al.* 2016). But it is in a recommended interval for AD.

The VS obtained in the work is in the range of (77.09–79.63), which is higher than the result reported for TWW (Andualem *et al.* 2016) and lower than the result reported by Tessfaw *et al.* (2020) for that waste. As is shown in Table 3 VS obtained from the mixture of TWW and biochar derived from Khat is in between the result of VS from TWW and Khat waste. The carbon-to-nitrogen ratio of biogas feedstock was determined using standard methods and the result obtained from TWW is in the range of (26.76–27.03). The ratio is within the optimum recommended range for the AD process, for biogas production.

Table 3 | Physicochemical properties of a mixture of tannery wastewater and biochar

Parameters	5% biochar addition to tannery wastewater	10% biochar addition to tannery wastewater	15% biochar addition to tannery wastewater	20% biochar addition to tannery wastewater
Moisture content (%)	91.52	90.20	88.88	87.56
TS (%)	8.48	9.80	10.12	11.44
VS (%)	77.09	77.94	79.63	78.78
Ash (%)	22.912	22.064	20.37	21.212
OC (%)	42.18	42.20	42.24	42.27
TN (%)	1.58	1.57	1.57	1.56
C/N ratio	26.76	26.85	26.94	27.03
pH	8.20	7.86	7.12	6.52
BOD5 (mg/l)	851.5	847	746	788
COD (mg/l)	3,401.29	2,487	1,527	1,656
Chloride (mg/l)	7.45	8.22	9.63	10.33
Sulfide (mg/l)	0.5	0.40	0.3	0.4
EC (mS)	9.87	10.57	11.68	12.72

3.2. Analysis of PH values and C/N ratios

The changes in pH have an effect on biological activity in AD. Changes in pH determine bacterial life found on the substrate in the digester. Each of the microbial groups involved in the reactions has a specific pH range for optimal growth and the optimum pH range. If the pH value is lower or upper than the optimum range, the biogas production rate is low. According to the reported result in the literature, the favorable pH range for methanogens is 6.3–7.8 (Lamb *et al.* 2019). In this study, the pH was between 6.72 and 8.20 in all digesters. All the digesters were within the optimum pH values. The minimum pH was observed in digester four and this could be due to biochar production at lower pyrolysis temperature (300 °C). Digester D1 (8.20) showed the highest pH followed by digester D2 (7.86). The best condition for biogas production was achieved at a ratio of (85%:15%) with an initial pH value of (7.12).

The proportion of carbon-to-nitrogen in organic matter is known as the C/N ratio. As the type, availability, and complexity of the substrate, all have an impact on the AD rate, this ratio is crucial in the AD processes. The carbon-to-nitrogen ratio of TWW is in the range of (26.76–27.03). This C/N ratio is within the optimum recommended range for the AD process, for biogas production. The optimum recommended range of C/N ratio for AD is 20–30:1 (Náthia-Neves *et al.* 2018). The variation of pH and C/N versus different percentages of the composition of biochar is shown in Figure 3. The uncertainty in pH was ± 0.01.

3.2.1. Analysis of TS, VS, and MC

TS content is one of the major factors that can affect AD process stability and the subsequent bioenergy production from the substrate. It affects the degradation rate of substrate, growth of bacteria, and treatment efficiency of the reactor. TS between 15 and 20% can be used as the recommended value for AD and within this range, hydrolysis and methane production dynamics match, the accumulation of inhibitors is also in a relatively moderate state (Zhao *et al.* 2021). Another result reported on the effects of TS content (TS between 2 and 10%) on the performance of sludge mesophilic AD, showed that the ultimate biogas yield firs increased and then decreased with the increasing TS. In this investigation, TS in the reactors were between 8.48 and 11.44%. The results obtained from this experimental test revealed that the digesters should be run at 10.12% TS since maximum cumulative biogas generation was obtained at this percentage total solid concentration. This result is almost similar to the result reported by Kelly Orhorhoro (2017), which was 10.16% of TS.

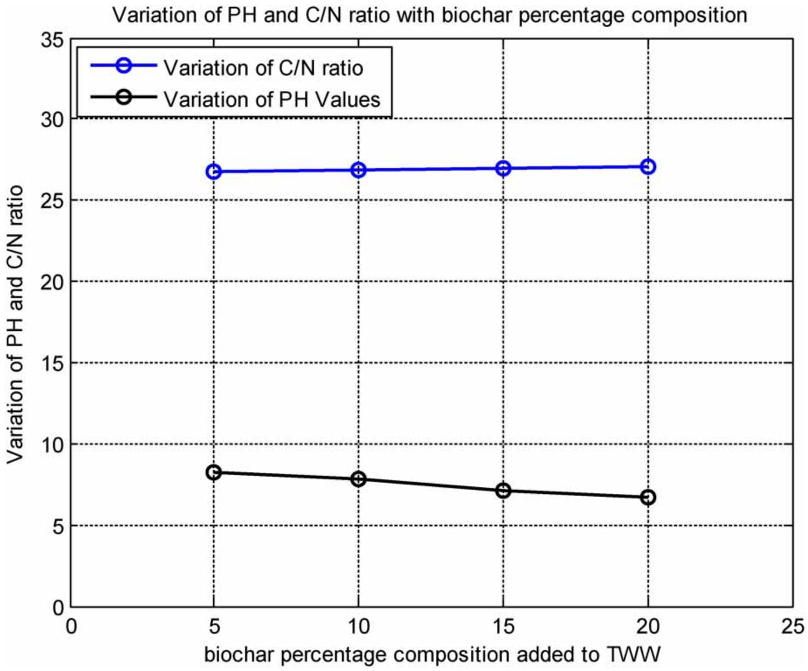


Figure 3 | Variations of pH and C/N with biochar percentage composition added to the TWW.

The most important parameter characterizing substrates for biogas production is VS content. It represents the fraction of solid materials that may be transformed into biogas (Presti *et al.* 2021). Since VS is an indicator of the potential for methane production, the specific methane yield on a VS base is not a constant in this experimental work. It was due to a mixture of TWW and biochar having a biodegradability fraction that ranges from 77.09 to 79.63%. The moisture contents of the mixture of TWW and biochar were between 87.56 and 91.52%. The graph of TS, VS, and MC versus the percentage composition of biochar added to the TWW is shown in the following Figure 4.

3.2.2. Salinity and electrical conductivity

In this experimental work, TWW has a high salinity content (9.57 g/l) and electrical conductivity (EC) (8.63 mS). This result is almost identical to the salinity and EC results that were previously reported (9.11.4 g/l) and (8.631.29 mS), respectively (Mekonnen *et al.* 2017; Tessfaw *et al.* 2020). The salinity ranged from 8.16 to 9.23 g/l and the average EC value ranged from 9.87 to 12.72 mS after biochar was added to TWW in the digesters. Due to the higher concentration of dissolved chemicals used in the tanning process and the conductive nature of the biochar added to TWW, the values of EC were high in all of the digesters. The variation of salinity and EC of the mixture of TWW and biochar are shown in the following Figure 5.

3.3. Evaluation of biogas production based on the mixing ratio

Biogas production potential and quality of the gas produced were evaluated at five different treatment combinations of TWW (TWW) and biochar (BC) using a bench-scale batch anaerobic digester. The following ratios were the five treatments used in the study; D1 (100% TWW), D2 (95% TWW: 5% BC), D3 (90% TWW: 10% BC), D4 (85% TWW: 15% BC), and D5 (80% TWW: 20% BC) on the basis of (mass basis). Each treatment was run in triplicate and 50 ml of inoculum was added to kick up the reaction.

The total amount of biogas produced by the system was calculated from the volumes of gas collector plastic bags. The volumes of the gas collector plastic bags were used to directly measure the amount of biogas produced, with the uncertainty in measurement of volume being ±1 ml and that of ±0.01% in biogas quality (methane content). Until the amount of gas produced peaked, the quality of the biogas was checked with a biogas analyzer. The calibrated biogas analyzer was directly connected to the plastic bag in which biogas filled during the volume measurement and the analyzer displayed the percentage of methane. The biogas produced from D1, D2, D3, and D4 were 350–520 ml, 500–680 ml, 600–760 ml, and 450–690 ml,

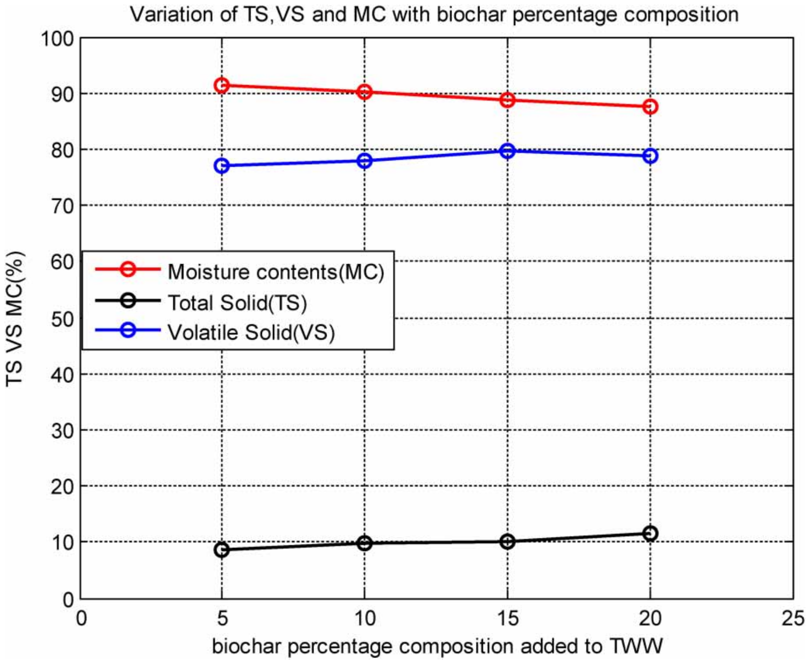


Figure 4 | Variations of TS, VS, and MC versus percentage of composition of biochar added to the TWW.

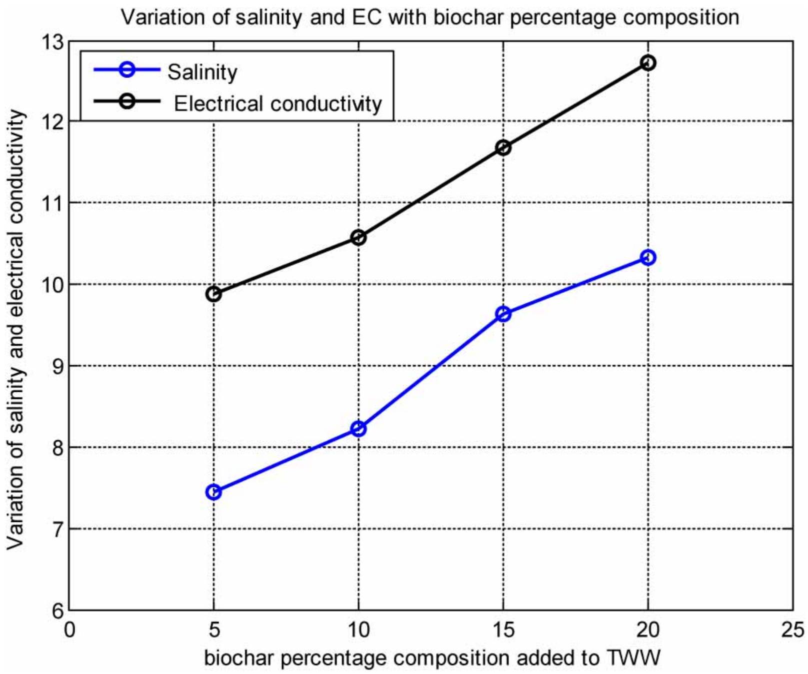


Figure 5 | Variations of salinity and EC with percentage composition of biochar.

respectively. As the percentage of biochar added to the digesters increased, the biogases produced from digesters D1, D2, and D3 increased. As the percentage of biochar increased to 20%wt, the biogas produced from D4 got reduced. Underloading and overloading of feedstock in the AD reactor have an effect on methanogenic bacteria. This reduction of biogas from D4 was due to acidogenic bacteria growing more quickly overall than methanogenic bacteria do at high organic loading rates, and inhibitory products like volatile fatty acids and H_2 build up in the reactor, which slows down the entire process. For optimum biogas yield, the required amount of feedstock must be added to the AD reactor (Maus *et al.* 2020). In these experimental tests the maximum cumulative methane production was obtained from D3 (85% TWW: 15% biochar). The cumulative biogas production trends were plotted in Figure 6(a) and the average and maximum cumulative biogas production is mentioned in Figure 6(b).

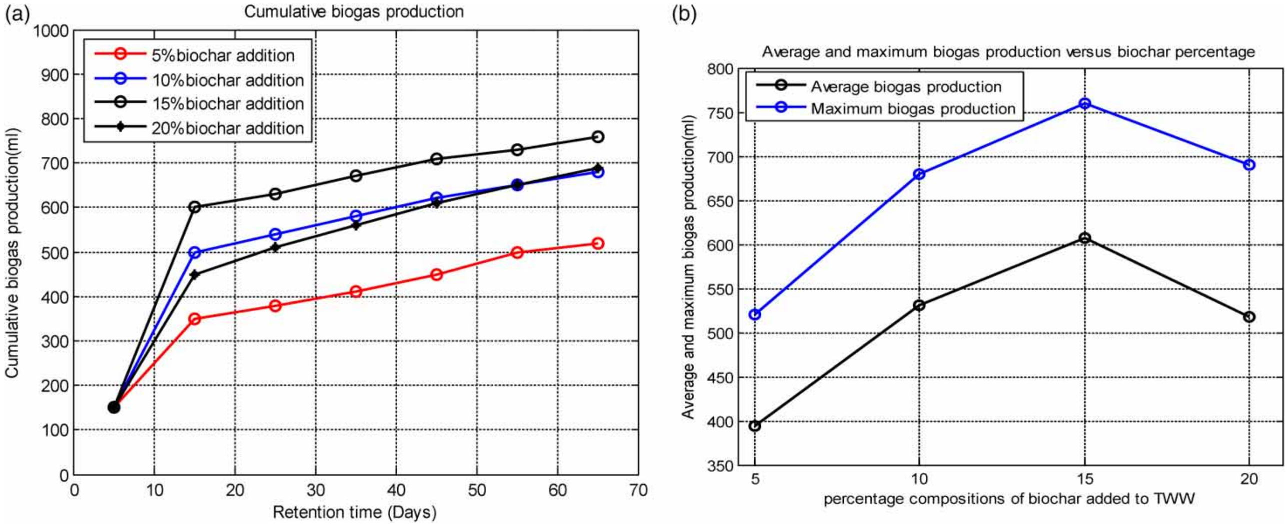


Figure 6 | (a) Cumulative biogas production and (b) average and maximum cumulative biogas production.

As shown in Figure 6(a), all the digesters started gas production on the fifth day and showed similar patterns until the 10th day of the experiment. At the beginning of the experiment biogas production rate was slow. This slow biogas production was primarily caused by the lag phase of microbial growth. The variations of biogas production in all digesters emerging started after 10 days of the experiments. The biogas production in D2 and D4 had no significant differences and between 50 and 65 days, had almost similar biogas production rates.

D3 has a significant difference in biogas production from the other three digesters after the 15th day of the experiments. This increment in biogas production was due to the correct percentage composition (dose) of biochar was added to the AD reactor (D3) which triggers the exponential growth of methanogens responsible for biogas production. Biochar is characterized by a large surface area, serves as a pH control agent (alkaline properties and counteracting reactor acidification), and its addition reduced the amount of H_2S that initially occurred in the headspace during reactor start-up, and may therefore have no impact on biogas and methane yields (Masebinu *et al.* 2022). A small amount of biogas was produced in D1 during the experimental period. It was due to the underloading of biochar percentage composition in the AD reactor (D1). Underloading and overloading of feedstock in the AD reactor have an effect on methanogens-forming bacteria (Orhorhoro *et al.* 2018).

As seen in Figure 6(b), the maximum cumulative biogas production was obtained at the digester containing (85% TWW: 15% biochar) which is D3. From 5 to 15% biochar addition on TWW, the average and maximum cumulative biogas production increased and from 15 to 20% biochar the average and maximum cumulative biogas production actually decreased. In this experimental test, the addition of biochar to the AD of TWW resulted in average and maximum cumulative biogas production varying in the range (435–578.33 ml) and (520–690 ml), respectively.

3.4. Effect of mixing ratio on bio-methane potential

In this study, the biogas amount and its composition were analyzed and recorded daily for 65 days. The methane yield profiles of batch experiments recorded can be seen in Figure 7(a). As seen in Figure 7(b), there were no notable differences in methane production in all digesters between the fifth and 10th days. The methane produced in D0, D1, D2, D3 and D4 were 17.04%, (18.50–41.20)%, (22.5–43.4)%, (27–51.6)%, and (20–48.6)%, respectively. These results are smaller than the methane produced from the fallen teak leaves biomass (Wannapokin *et al.* 2017), ensiled Napier grass (Dussadee *et al.* 2017), pretreated fallen teak leaves (Wannapokin *et al.* 2018), crushed water hyacinth combined with swine dung (Unpaprom *et al.* 2021), co-digestion of water primrose with cow dung (Nong *et al.* 2022a, 2022b), and Ludwigia hyssopifolia (Nong *et al.* 2022a, 2022b). However, the present yield results seem higher than the methane produced from mono-digestion of the TWW. As can be seen from the figure, all of the digesters had low methane at the start of the experiment. This might be caused by the methanogenic bacteria's slow acclimatization. Between the 25th and 35th days, the methane in digesters D2 and D4 was almost similar and D1 and D2 had significant differences.

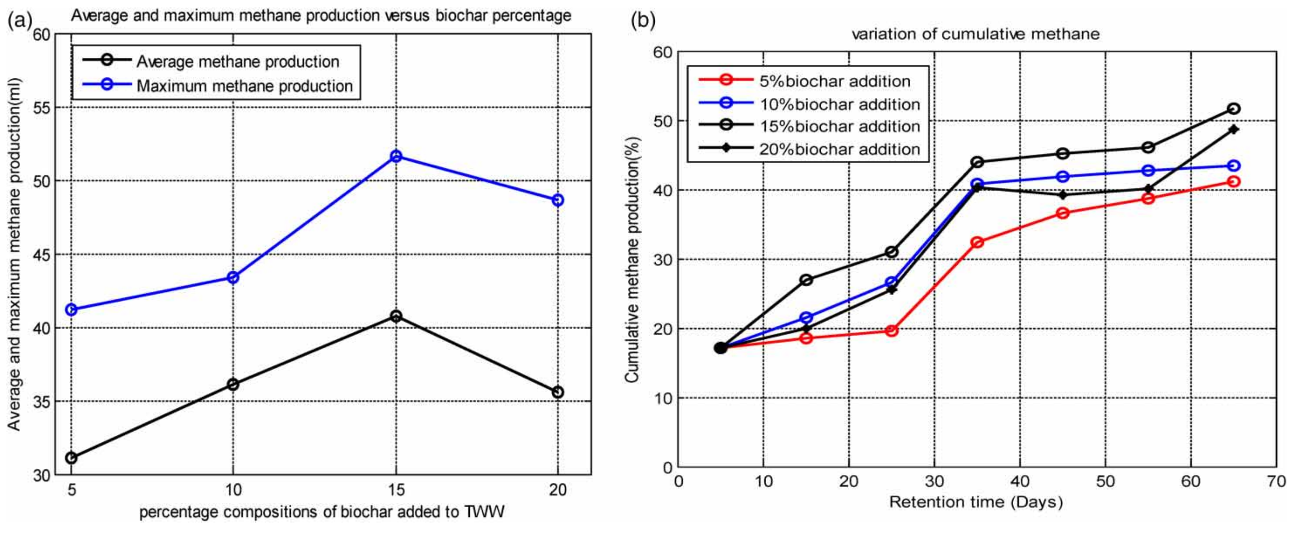


Figure 7 | (a) Variations of average and maximum cumulative methane production (%) and (b) variations of cumulative methane content.

In D3 the maximum methane production was observed at the end of this experimental test (55th–65th) which was 51.6%. This results in three times the methane produced from digester D0 (without biochar). This increment in methane production was due to adding an optimal dose of biochar in the AD reactor (D3) which enhances the exponential growth of methanogens responsible for biogas production. Adding an optimal dose of biochar significantly enhanced the efficiencies of hydrolysis, acidogenesis, and acetogenesis and it mediates interspecies electron transfer selectively enriched electroactive fermentation bacteria (Ma *et al.* 2021; Shi *et al.* 2022). A correct dose of biochar addition inhibited acetic acid production in the anaerobic fermentation system and promoted methane production based on hydrogen and carbon dioxide levels. An appropriate dose of biochar addition to AD facilitates the direct interspecies electron transfer between fermentative bacteria and electro-trophic methanogens and enhances methane production (Pan *et al.* 2019).

A smaller cumulative methane production was observed in D1. This smaller methane production was due to under loading of biochar dose in D1. The methane production was reduced in D4. This reduction of methane was due to excessive biochar dose added to the AD reactor (D4). Excessive biochar dose caused negative effects with methanogenic efficiency and lag phase prolonged and inhibitory effects were observed at high dosages (Pan *et al.* 2019). The amount of methane produced by digesters D1, D2, D3, and D4, increased by 58.64, 61.1, 66.98, and 64.94%, respectively, in comparison to the quantity of methane produced by digester Do.

As seen from Figure 7(b), the maximum cumulative methane production was obtained at the digester containing (85% TWW:15% biochar) which is D3. From 5 to 15% biochar addition on TWW, the average and maximum cumulative methane production linearly increased, and from 15 to 20% of biochar addition on the average and maximum cumulative methane production as such reduced. This reduction in methane production was due to overloading of biochar to the digester. In this experimental test, the addition of biochar to the AD of TWW resulted in average and maximum cumulative methane production varied in the range 31.13–35.6 and 41.2–51.6%, respectively.

As can be observed from Figure 8, the calculated errors for cumulative methane are in the acceptable range ($P > 95$ confidence interval).

4. CONCLUSIONS

Biogas production from TWW has challenges due to chemicals used during leather tanning. In this work, the effects of the addition of biochar, made from Khat waste at a pyrolytic temperature of 300 °C, in different percentage compositions on AD of TWW, collected from Modjo tannery Share Company were investigated for 65 days to evaluate bio-methane production efficiency at a constant mesophilic temperature of 38 °C. The results showed that for the five experimental tests 0, 5, 10,

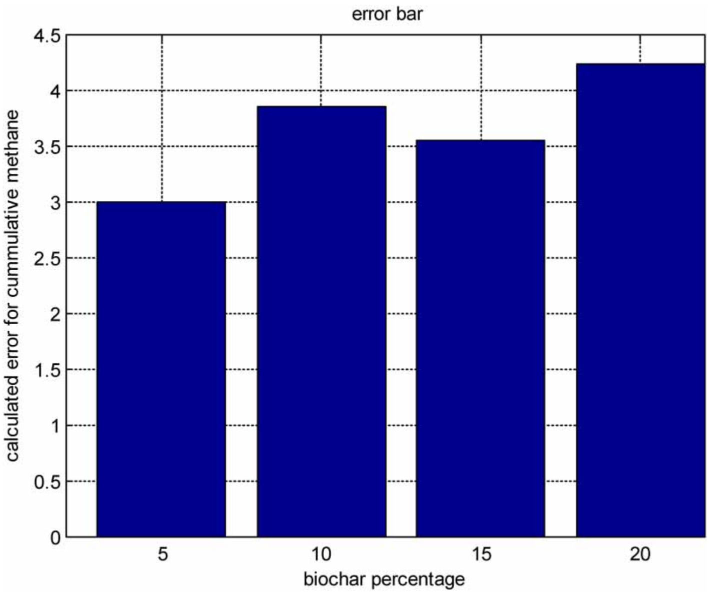


Figure 8 | Calculated error percentage in cumulative methane content.

15, and 20% biochar addition to TWW generates a three-fold increase in methane compared to the control (without biochar). The quality and quantity of the biogas yield is found to be the maximum at 15% biochar addition at 760 ml and 51.6% methane content. The results from this study show a higher yield with biochar addition than the mono-digestion of TWW. According to this study, it can be concluded that the addition of an appropriate dose of biochar on AD can improves the efficiency of methane production. The effects of biochar addition to AD of TWW especially in the area of energy generation have not yet been adequately investigated and further research is still required to comprehend and enhance AD of TWW.

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AUTHOR CONTRIBUTIONS

S.K.A. and V.R.A. conceptualized the study; S.K.A. and N.G.H. worked on the methodology and formal analysis and data curation; S.K.A. and V.R.A. developed the original draft; S.K.A., V.R.A., N.G.H., and L.S.S. reviewed and edited the draft. All authors have read and agreed to this version of the manuscript.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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