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Sustainable green biogas production from pretreated wheat straw blended with coffee husk using neem leaves-based iron (III) nanocatalyst via response surface methodology

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Abstract

The present study investigated the enhancement of wheat straw and coffee husk waste used as a biogas source for energy production using iron nanocatalysts from neem leaf extract. In line with this the synthesized neem leaves extract of Iron nanocatalyst was characterized for the morphological and functional group. To achieve this, thermal acid pretreatment was carried out using equal proportions of blended wheat straw with coffee husks and subjected to the anaerobic digester with 0.3 g/L of neem leave extract Fe–O nanocatalyst to improve biogas production. The influence of temperature, the concentration of Sulfuric acid, and cooking time during the pretreatment to improve biogas yield was investigated. Response surface methodology of Box–Behnken Design (BBD) during the thermochemical pretreatment is employed. The biomass was pretreated at 160 °C temperatures, 3% concentration of sulfuric acid, and 30 min of cooking time. The highest cumulative biogas and biomethane obtained from the biomass were 764 mL/g and 460 mL/g Volatile solid. Augmentation of neem leaves extract of Iron nanocatalyst enhanced the methane gas yield with volatile solids up to 89.5%. Therefore, the use of pretreatment for the catalysis of lignocellulose substrates is advantageous for the creation of a process that is both economical and environmentally friendly. The produced biogas energy could be used as a substitute for fossil fuels for various purposes while mitigating important environmental pollution problems and enhancing sustainable energy utilization. In considering 'waste to energy' for the production of sustainable energy from waste and fulfilling the energy demand is possible.

Keywords Biogas · Coffee husk · Wheat straw · Nano catalyst · Thermochemical pretreatment

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Introduction

Today, energy is a captious and critical resource for the world densely populated which consumes renewable and non-renewable resources. One of the challenges facing the world today is dealing with all kinds of waste and energy crises [1]. Rapid population growth, turbulent and disorderly urbanization have created serious problems with energy demand and waste disposal [2]. The shortage of fossil fuels for the population grows as the population grows faster. To meet these challenges, various researchers are trying to improve green energy from various sources, non-polluting and renewable by various technologies [3, 4]. Thus, Organic matter can be separated into highly biodegradable compounds, such as carbohydrates, lipids, and proteins, and less biodegradable compounds, such as lignocellulosic biopolymers [5]. In addition to this, global warming, urban pollution, depletion of oil reserves, and the high cost of fossil fuels are driving research into alternative energy sources, especially existing biomass. Biomass energy can be derived come from a variety of sources, including agricultural, food, forestry residues, waste, and animal waste [6].

The production of biogas from organic waste has gained popularity in recent years and has become an accepted practice mainly due to its energy requirements and the proper treatment of organic waste without harming humans and the environment [7]. Biogas is a form of green energy that consists of methane as the major compound composition (50–75%), carbon dioxide as a second major component (25–45%), and other gaseous traces of material produced from the decomposition of organic matters through four steps of anaerobic digestion process consequently hydrolysis, acidogenesis, acetogenesis, and methanogenesis stages [8]. In line with this**,** biogas units can contribute significantly to sustainable development in rural areas, as well as provide farmers with new income opportunities [9].

Nowadays, different biomass resources used in digesters are depending on raw materials such as agricultural waste, food waste, sewage, and industrial waste [10]. Among these resources, preprocessed lignocellulose materials are easily available biomass materials. They are also suitable for renewable resources and eco-friendly environments. These biomass materials have the capacity to produce bioenergy that is used for different activities such as heat, power, heat, transport fuels, and injection to gas pipelines [7, 11]. It is estimated that 33% of all agri-food production is lost in the form of waste [12]. The complex organic matter of lignocellulosic biomass of agricultural wastes is converted to biogas energy by different methods to limit the rate of anaerobic degradation [13, 14]. In the past few years, several pretreatment techniques used to convert lignocellulosic material to biomass energy have been researched, including steam explosion, alkali, acid, ammonia fiber explosion, and organic solvents, and can be applied to increase biogas production. The waste can be co-digested with other waste for a synergistic effect, and cost-effective anaerobic digestion to improve biomethane production [5, 15].

However, the dissolution of organic matter affects pretreatment which is used to improve the efficiency of the hydrolysis step in anaerobic digestion [16, 17]. In addition to this, the increase in the surface area of the solids is due to biomass solubilization and the breakdown of fiber structures, like lignin [18–20]. To solve these challenges, thermal pretreatment (temperature/pressure and steam explosion) combined with chemical (Acid and Alkali) pretreatment method breakdown polymers, releasing monomers and other degradation products in a liquid medium formed by the solubilized matter and the steam condensation [17]. These pretreatment techniques are easily available and simple for operating and microbial (enzymatic) pretreatment of natural lignocelluloses. Longer pretreatment time can be required to grow the substrate and exhibit lignolytic properties [19, 21]. However, applying the combined pretreatment for the conversion process is useful in producing more biogas than using the single pretreatment. Because, it solubilizes lignocellulosic components of the structure based on temperature and moisture content and makes the lignocellulosic material easily exposed for the hydrolysis step, and avoids the formation of inhibitors and enhance the amount of cellulose that can be used to make value-added commodities [22, 23]. Acid treatment followed by thermal pretreatment is carried out for several hours and is used to improve hemicellulose hydrolysis does not produce inhibitors. In addition to producing renewable biomethane, the most promising important is converting agricultural waste to valuable products is one of the most environmental concerns [22]. In developing countries like Ethiopia, wheat straw, teff straw, barley straw, and coffee husks are the waste that is placed and burned in landfill causing to change in climate [24]. Thus, co-digestion can better balance micro and macronutrient due to the availability of certain concentrations of these nutrients in feedstock [11, 25]. Furthermore, the co-digestion of mixed waste also supports different bacterial and methanogenic pathways [17, 26]. To accelerate the process of converting waste mixtures into products in an anaerobic plant, a catalyst in which nanocatalyst activity plays a key role to increase methane production [27]. Recent research has shown that adding nanoparticles can improve biogas production and impact the anaerobic digestion process. Nanocatalysts such as Cu, Ni, and Co are nanoparticles used to improve the conversion rate of mixed feedstocks to biogas through anaerobic digestion. These metal nanoparticles take a longer time to break down and are sometimes risky to the climate. In this context, green nanotechnology enhances production technology and is attracting the attention of the biofuels and bioenergy sectors. Due to their inexpensive price and processing properties that are similar to those of other metallic nanocatalysts, nanocatalysts made utilizing green technology are chosen. To account for this, the present study investigated the green synthesis of iron nanoparticles from neem leaf extract contains a variety of biologically active substances that act as reducing and capping agents and help stabilize nanoparticles, including terpenoids, sitosterol, polyphenolic flavonoids, saponins, and alkaloids carried out by biological means [28]. After biogas production from nano-catalyzed degradation, the remaining sludge is treated as a biological fertilizer Statistical experimental design techniques like Response Surface Methodology are used to investigate the effects of the variable on the pretreatments of biomass for improvement of biogas production. Box-Behnken Design is the type of Response Surface Methodology that is applied to build models and investigate individual and interaction effects of the selected operating condition on the given response in a given experiment [29].

The main objective of this work is to analyze the potential impact of wheat straw and coffee husk on biomethane gas through anaerobic digestion by using iron nanoparticles from neem leaf extract. Additionally, to investigate the effect of temperature, acid concentration, and retention time of hydrolysis during pretreatment on the yield by using the Box-Behnken Design.

Materials and methods

Material and reagents

Wheat straw and coffee husks were collected from Jimma agricultural research center, Oromia, Ethiopia in April 2022. The chemical sulfuric acid with a purity of 98 % was collected from Chem-Supply Kirkos Ltd. in Addis Ababa, Ethiopia. The chemical of pure analytical grade was used.

Analysis of physiochemical properties of wheat straw and coffee husk

The collected biomass was crushed in a domestic mill until an average particle size of 1 to 2 mm to ensure biomass homogeneity before pretreatment. Also, the solid fraction (total solids and volatile solids), (total and soluble), and pH of all samples (raw and pretreated biomass) were determined following the Standard Methods (APHA, 2005). The cellulose, lignin and hemicellulose content of the biomass was determined according to the method ASTM D 5896-96 [21].

Thermo-chemical pretreatment of biomass

Thermal acid pretreatment was carried out using 200 g of wheat straw and coffee husks in equal proportions. The pretreatment of wheat straw and coffee husks with thermal acid was carried out in a 600 mL stainless steel reactor fitted with a Teflon cartridge. In this pretreatment reactor, a pretreated sample is added, followed by the addition of sulfuric acid based on the typical thermochemical pretreatment performed in the presence of heat. Finally, acid heat pretreatment was performed at different temperatures, and sulfuric acid concentrations and time combinations were evaluated. Therefore, all pretreatment conditions produced granular and soluble biomass fractions.

Synthesis of iron oxide nanoparticles from neem leaves extract

Neem leaves were collected around the town of Jimma. To remove dust particles, neem leaves were washed through distilled water and dried at room temperature. Then, after grinding the leaves to a fine powder, 10 g of the leaf powder was transferred to a conical flask containing 200 mL of sterile distilled water and boiled for 15 min at 80 °C.

The extract was then filtered and centrifuged at 5000 rpm for 10 min. Finally, the filtered neem leaf extract solution that was green and clear was collected for further use.

To synthesize the Iron Oxide Nanoparticles, a 1:1 ratio of the mixture of Neem leaf extract and 0.03 M of Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) solution will be dissolved in 100 mL of sterile deionized water. Then, the solution was transferred to the heater equipped with a magnetic stirrer and heated at 80 °C for 20 min until the brownish-black color (indicates the synthesis of iron oxide nanoparticles) was formed and the resulting mixture was cooled at room temperature. Finally, the obtained black powder will be lyophilized overnight and characterized by FTIR, and XRD pattern.

Anaerobic digestion of pretreated blended wheat straw with coffee husk

Digested manure was used as an inoculum in the present work. The inoculum was prepared according to the method provided by [22]. It was collected from a local biogas plant digesting cow dung in Jimma biogas plant. The feed port, and gas collector equipped with 600 mL glass bottles were used for anaerobic digestion of blended pretreated wheat straw with coffee husk (1:1 ratio), and 0.3 g/L of neem leave extract Fe–O nanocatalyst and investigate their biomethane potential (BMP). The pH of all anaerobic bioreactors was controlled over time and the temperature was maintained at 35 ± 0.5 °C for 47 days. For each anaerobic digestion, the biogas cumulative production experiment was studied in four categories-untreated biomass, pretreated biomass at different temperatures, percentage concentration of sulfuric acid, and cooking time. The percentage of CH_4 content in the generated biogas was determined by utilizing a gas analyzer (Biogas 5000, Geotech, India).

Analytical parameter

Analyses for total solids (TS), and volatile solids (VS) of wheat straw and coffee husk were carried out according to standard methods.

$$TOC = \frac{VS \times TS}{0.018}$$

$$VS = \frac{VS_{added} - VS_{removed}}{VS_{added}}$$

Here VS (added) = volatile solids added in grams at the start of the experiment and VS (final) = volatile solids remaining after the completion of an experiment. VS removal = VS removal is digested volatile solids after an anaerobic digestion experiment of 47 days.

Experimental design

The production of biogas from wheat straw blended with coffee husk was analyzed by using Design-Expert software version 13.0.5.0. Response Surface Methodology of Box-Behnken Design (BBD). Each parameter is considered at three different levels to determine the effects of thermochemical parameters on biogas yield. The independent variables namely temperature (140, 160, and 180 °C), retention time (10, 30, and 60 min), and H_2SO_4 acid concentration (1.5, 3, and 4.5%), and dependent variable as biogas yield were investigated.

Results and discussion

Biomass characterization

The characterization result of biomass of wheat straw and coffee husk is shown in Table 1. The result depicts that wheat straw contained higher total solids (TS), hemicellulose, and lignin, compared to the Coffee husk. However, the wheat straw has a lower content of cellulose, VFA, TOC and TKN when compared to Coffee husk. C/N ratio of wheat straw was higher than coffee husk due to lower nitrogen content. This can help to stabilize the C/N ratio when co-digested with coffee husk and cow dung for inoculant. The pH values of both wheat straw and coffee husk shows acidic condition due to high nitrogen content in the form of undigested protein. As seen in the analysis, the biomass has a larger percentage of C, O, and H contents, demonstrating the straw's higher calorific value and higher energy potential. However, because C is much higher than N, the C/N ratio for the anaerobic digestion of straw is also very high, indicating a deficiency in a nitrogen source.

Transform infrared (FTIR) analysis

Fig. 1 shows the results of the FT-IR analysis of wheat straw and coffee husk. As shown in Fig. 1a, Fourier transform infrared (FTIR) spectroscopy determined the highest peak is at 3500 cm^{-1} and the lowest peak is around 3125 cm^{-1} which depicts

Table 1 Characteristics of raw substrates

Parameters	Wheat straw	Coffee husk
pH	5.8 ± 0.1	5.9 ± 0.2
Total solids, TS, (%)	93 ± 0.25	90 ± 0.4
Volatile solids, VS, (%)[a]	79.4 ± 0.23	92 ± 0.7
Total organic carbon, TOC, (%)[a]	52.7 ± 0.11	55.6 ± 0.2
Total Kjeldahl Nitrogen, TKN, (%)[a]	2.11 ± 0.11	3.5 ± 0.3
Carbon to nitrogen ratio, C/N	44.2	32.2
Cellulose (%)[a]	38.5 ± 0.3	40.2 ± 0.1
Hemicellulose (%)[a]	29.6 ± 0.4	22.5 ± 0.3
Lignin (%)[a]	17.1 ± 0.2	16.1 ± 0.25
volatile fatty acids, VFA, (mg/L)	235 ± 6	290 ± 2
Total alkalinity, TA, (mg/L)	1149 ± 8	1210 ± 3
VFA/TA	0.17	0.21

[a] % of TS

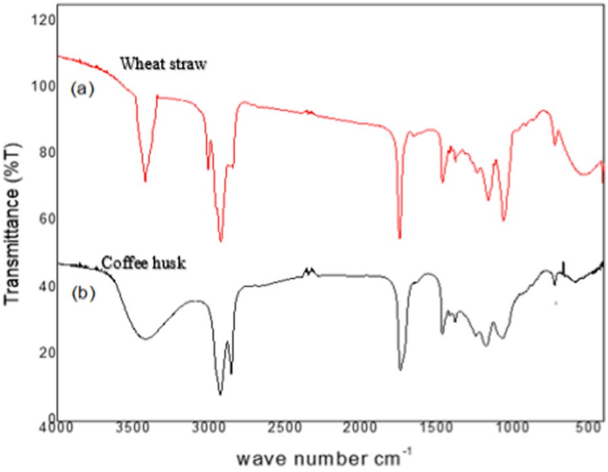

Fig. 1 Fourier Transform Infrared spectra (FTIR) analysis of (a) wheat straw (b) coffee husk

they are both in the single bond region in the wheat straw. A slightly broad peak around the wavenumber of 3500 cm^{-1} was attributed to the OH stretch bond which illustrates the existence of alcohol and phenols; while at 3125 cm^{-1} there was a C–H stretch bond that shows the existence of an aromatic ring [12, 15]. In this study, Fourier transform infrared (FTIR) spectroscopy successfully confirmed the carbonate group which attributed around the peak at 1400, 870, and 710 cm^{-1}.

Fig. 1b shows the presence of functional groups of different compounds found in the coffee husk in the range of 400–4000 cm^{-1}. Thus, the band observed between 3650 and 3120 cm^{-1} is associated with hydroxyl (OH) and carbonyl functional groups, while the weak bands at the region of 2920 cm^{-1} dispensed to asymmetric C–H stretching. On the other hand, the peak observed in the region between 1700 cm^{-1} and 1490 cm^{-1} were assigned to C=C of pyrone and C=O of carboxylic groups correspondingly. In addition to this, the functional group of C–O present in compounds like carbonyls, ketones, aldehydes, or ester groups were observed to peak at 1632 cm^{-1} in the aromatic region [28]. The peak in the range of 1200–900 cm^{-1} have also been associated to either Si–O or C–O stretching in alcohol and ether.

Effects of thermochemical on compositional change of biomass of wheat straw and coffee husk

The effective pretreatment processing ensures that highly producing the biomethane from the lignocellulose biomass. As it has been shown in Table 2 by using combined thermal and chemical pretreatment, more cellulose was produced at 160 °C for 30 min with 3% concentration of H_2SO_4. At these conditions, the cellulose of wheat straw and coffee husk was increased by 36.36% and 35.8% when compared with untreated biomass. At these conditions, 23.54% of hemicellulose and 21.05% of lignin is decreased for wheat straw. Similarly, 21.56% of hemicellulose and 21.4%

Table 2 Effects of temperature on compositional changes due to thermochemical pretreatment of wheat straw and coffee husk at constant sulfuric acid concentration (3%) and time (30 min)

Biomass	Pretreatment condition [Temperature]	Cellulose content %	Cellulose increment %	Hemicellulose content %	Hemicellulose lowered %	Lignin content %	Lignin lowered %
Wheat straw	Untreated	38.5 ± 0.82	–	29.6 ± 0.29	–	17.1 ± 0.92	Untreated
	140	41.2 ± 0.22	7.01 ± 0.23	26.2 ± 0.42	11.48 ± 0.51	15.2 ± 0.63	11.11 ± 0.19
	160	46.3 ± 0.23	20.59 ± 0.21	24.25 ± 0.3	18.07 ± 0.89	14.02 ± 0.61	18.01 ± 0.78
	180	52.5 ± 0.11	36.36 ± 0.22	22.63 ± 0.62	23.54 ± 0.96	13.5 ± 0.22	21.05 ± 0.25
Coffee husk	Untreated	40.2 ± 0.43	–	22.5 ± 0.55	–	16.1 ± 0.81	–
	140	42.5 ± 0.77	5.72 ± 0.65	20.5 ± 0.32	8.89 ± 0.42	15.1 ± 0.31	12.42 ± 0.74
	160	Untreated	40.2 ± 0.43	–	22.5 ± 0.55	–	16.1 ± 0.81
	180	54.6 ± 0.73	35.82 ± 0.74	17.2 ± 0.47	21.56 ± 0.46	12.6 ± 0.45	21.4 ± 0.56

of lignin is decreased for coffee husk. This result indicates that more glucose was produced during the hydrolysis process, which played a significant role to facilitate more production of methane gas. The cellulose content of untreated wheat straw and coffee husk in the present study was shown in Tables 3 and 4. It is comparable to that of other lignocellulosic biomass such as rice straw (35–44%) and corn stover (40%) as reported in the literature [11]. This adverse result might be attributed to a potential loss of biodegradable matter that occurred during the pretreatment, namely proteins, and fats.

The changes in the composition of lignocellulosic biomass can be because of the sulfuric acid hydrolysis that generates hydronium ions due to its auto-ionization. The generated hydronium ion (H_3O^+) has the capability to vitiate and broke the bond of the lignocellulosic biomass since the acid ion act as a catalyst. The heterocyclic ether bonds of hemicellulose are susceptible to this type of reaction. Because it causes both the generation of oligosaccharides and the splitting of the acetyl groups from the hemicellulose [17]. Due to the principle of hydronium ions acting as catalysts the lignocellulose material was converted into a simple sugar that was used for producing more cumulative biogas.

As it has been shown in Tables 3 and 4, when the hydrolyze time rise to 60 min the cellulose content was increased and the surface of each biomass was distorted and exploited. This is because more sulfuric acid was dispersed into biomass and constantly heated to convert to furfural. This helps us to volatile organic acids, and feasible their loss by volatilization. Moreover, considering the total solid reduction, dissolved lignin can be re-condensate on the surface of the particulate biomass for pretreatment conditions greater than 150 °C.

Therefore, the reduction in the soluble organic matter on the most severe pretreatment could be a consequence of the volatilization of byproducts. The re-condensation of the dissolved lignin on the solid fraction has a direct consequence for the process's aggressiveness.

Characterization of iron oxide nanocatalyst

Fig. 2 depicts the results of the FT-IR analysis of the iron oxide nanocatalyst prepared from neem leaf extract through biological treatment. As shown in Fig. 2, the reaction between the iron salt and the neem leaf extract has occurred. This is due to the presence of the peak formation at 3342 cm^{-1} for the OH stretch of a hydroxyl group of alcohols. The N–H stretching and bending vibration of amine group NH_2 and OH, as well as the overlap of the stretching vibrations attributable to water and the phenolic group in neem leaf extract molecules, are demonstrated by the strong stretching band that appears approximately 3342 cm^{-1} (Fig. 2). The peak at 1616 cm^{-1} represents for C=O group held accountable for the equilibrium of neem leaves-iron nanocatalyst and 1057 cm^{-1} indicates the presence of sulfonates [30]. In line with this, the peak at 513 and 533 cm^{-1} describes the existence of iron oxide in the reducing solutions. This discovery demonstrated that Fe–O nanocatalysts were produced in a one-pot process via neem leaf mediation.

Table 3 Effects of sulfuric acid concentration on compositional changes due to thermochemical pretreatment of Wheat straw and coffee husk at constant temperature (160 °C) and time (30 min)

Biomass	Pretreatment condition [H_2SO_4]	Cellulose content (%)	Cellulose increment (%)	Hemicellulose content (%)	Hemicellulos e lowered %	Lignin content (%)	Lignin lowered (%)
Wheat straw	Untreated	38.5 ± 0.11		29.6 ± 0.19		17.1 ± 0.52	
	1.5%	41.5 ± 0.12	7.01 ± 0.64	27.2 ± 0.22	11.48 ± 0.58	15.2 ± 0.39	11.11 ± 0.83
	3%	47.3 ± 0.52	20.59 ± 0.21	25.25 ± 0.57	18.07 ± 0.71	13.02 ± 0.79	18.01 ± 0.47
	4.5%	52.8 ± 0.23	36.36 ± 0.84	23.63 ± 0.88	23.54 ± 0.41	12.9 ± 0.85	21.05 ± 0.65
Coffee husk	Untreated	40.2 ± 0.35	–	22.5 ± 0.44	–	16.1 ± 0.99	–
	1.5%	42.8 ± 0.41	5.72 ± 0.98	21.3 ± 0.54	8.89 ± 0.85	14.5 ± 0.93	12.42 ± 0.21
	3%	46.9 ± 0.12	18.02 ± 0.38	18.02 ± 0.81	15.11 ± 0.12	13.2 ± 0.65	15.53 ± 0.59
	4.5%	53.98 ± 0.23	35.82 ± 0.34	17.6 ± 0.98	21.56 ± 0.32	12.4 ± 0.52	21.4 ± 0.27

Table 4 Effects of time on compositional changes due to thermochemical pretreatment of wheat straw and coffee husk at constant temperature (160 °C) and sulfuric acid concentration (3%)

Biomass	Pretreatment condition [time]	Cellulose content %	Cellulose increment %	Hemicellulose content %	Hemicellulose lowered %	Lignin content %	Lignin lowered %
Wheat straw	Untreated	38.5 ± 0.5		29.6 ± 0.25		17.1	
	10 min	40.9 ± 0.47	6.23	26.2 ± 0.56	11.48 ± 0.78	16.2 ± 0.18	5.84 ± 0.95
	30 min	44.3 ± 0.47	15.06 ± 0.52	25.25 ± 0.21	14.7 ± 0.62	14.02 ± 0.55	18.01 ± 0.24
	60 min	51.5 ± 0.54	33.77 ± 0.84	22.3 ± 0.55	24.66 ± 0.22	13.5 ± 0.451	21.05 ± 0.16
Coffee husk	Untreated	40.2 ± 0.65	–	22.5 ± 0.41	–	16.1 ± 0.11	–
	10 min	41.9 ± 0.69	4.23 ± 0.37	20.5 ± 0.57	8.89 ± 0.86	14.9. ± 0.20	7.45 ± 0.35
	30 min	47.5 ± 0.21	18.02 ± 0.19	19.03 ± 0.38	15.11 ± 0.49	13.6 ± 0.35	15.53 ± 0.42
	60 min	53.6 ± 0.43	33.82 ± 0.11	17.4 ± 0.29	21.26 ± 0.27	12.1 ± 0.64	24.84 ± 0.21

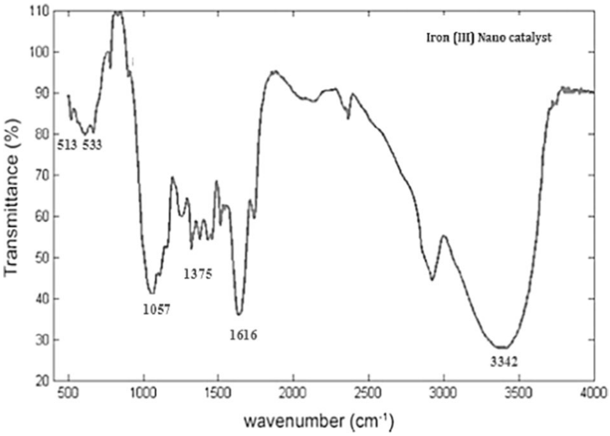

Fig. 2 FT-IR analysis of synthesized Iron oxide Nao catalyst

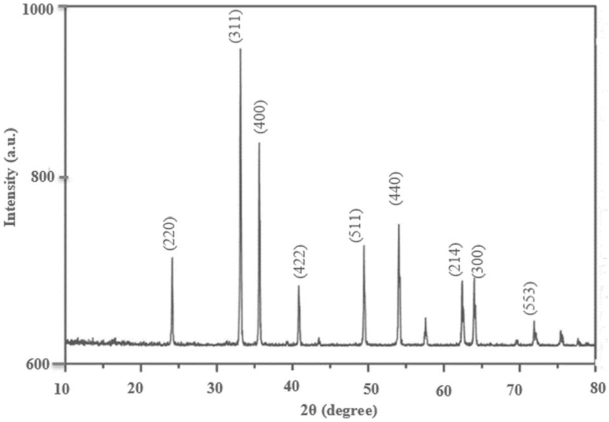

Fig. 3 X-ray diffraction (XRD) patterns of powdered iron oxide nanocatalyst

The XRD pattern of Fe–O Nano catalysts synthesized via neem leaves extract was revealed by powder X-ray diffraction measurement as illustrated in Fig. 3. It reveals that the agreement of neem leaf extract Fe–O nanocatalysts with the magnetite cubic crystalline Fe nanoparticles. The peaks studied by the XRD plot (220) (311) (400) (422) (511) (440) (214) (300) (553) are identical to the normal diffraction of the iron structure (JCPDS No. 01-089-0950). This shows that the synthesized iron nanoparticles are free of impurities [31, 32]. The average crystal size of neem leaf extract Fe-O Nano catalysts ranges from 3.07 ± 0.75 to 6.14 ± 0.9 nm found from the Debye–Scherrer equation. From the XRD analysis, there is a formation of clear phases for Iron oxide, which implies the synthesis of crystalline Nanocatalyst. It was clear from the strong and distinct peaks that the

Fe–O-nanocatalyst produced by the reduction of iron ions using neem leaf aqueous extract was extremely crystalline in composition.

Augmentation of biogas production from pretreated wheat straw blended with coffee husk

The most important parameter evaluated at the end of 47 days of the experiment was volatile solid matter (VS) which is directly proportional to the amount of cumulative biogas produced. From the three experiments, the volatile solids were determined at different temperatures, cooking time, and percentages of concentration of H_2SO_4. In addition to this, there was the enhancement of biogas occurred due to the addition of Fe–O nanocatalyst. It was observed that the greatest biogas yield was obtained in the bioreactor supplemented with Fe–O nanocatalyst compared to the reactor supplemented with untreated bulk biomass material. The augmentation of neem leaf extract of Iron oxide nanocatalyst showed the lessening in the lag phase and caused an increment of the methane production from onwards.

As shown in Fig. 4, the composition of biogas shows good results with high CH_4 and CO_2 content and trace amounts of other gases of 4.2%. However, for the untreated biomass, the proportion of other gases increased to 8.9%. This indicates that the biodegradation of untreated biomass produces biogas with high content of impurities. This may limit the use of these gases for various purposes sensitive to impurity proportions.

The methane gas obtained during treatment at temperatures of 140, 160 and 180 °C were 379, 459, and 415 mL/g at 30 min, and 3% of the concentration of sulfuric acid from cumulative biogas. On the other hand, the cumulative methane from this second anaerobic digestion was 361, 459, and 403 mL/g was produced

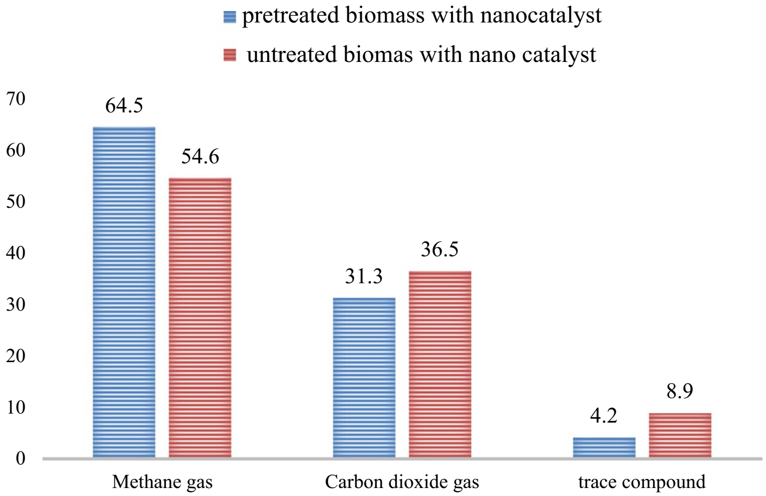

Fig. 4 CH_4 and CO_2 percentage yield from untreated and pretreated biomass with nanocatalyst using a gas analyzer

from the pretreated mixture biomass of wheat straw and coffee husk. This was achieved at 1.5, 3, and 4.5% of sulfuric acid at a fixed temperature (160 °C) and time (30 min). In addition to this, the cumulative methane from this third anaerobic digestion was 348, 458, and 386 mL/g VS was produced from pretreated mixture biomass of wheat straw and coffee husk at 10, 30, and 60 min at constant temperature (160 °C) and 3% of sulfuric acid concentration.

The removal percentage of volatile, solids of the mixture of pretreated biomass at the temperature of 140,160 and 180 °C were 49, 84, and 75.5%. The biomass mixture was pretreated at 160 °C temperature with different concentrations of sulfuric acid (i.e., 1.5, 3, and 4.5%) and hydrolysis times of 10, 30, and 60 min of cooking time were 43, 62, and 89.5%. At these conditions, the obtained volatile solids were 42, 59, and 78.5%. This is due to the radicals produced in the aqueous phase can attack the hemicellulose chains, the solubilization of hemicelluloses may increase with increasing delignification and could result in the solubilization of both the lignin and hemicelluloses complex's constituents.

Analysis of variances (ANOVA) of biogas yield

Based on the analysis of variance (ANOVA), the parameter, which significantly affected the biogas yield, was shown in Table 5. From this table, the Model F-value of 376.41 implies the model is significant, P-values less than 0.0500 indicate model terms and all factors are significant and the lack of fit F-value of 0.5536 implies the lack of fit is not significant.

Table 5 ANOVA analysis for process parameter

Sources	The sum of the squares	The sum of the mean	F-value	P-value	
Model	73,493.26	8165.92	376.41	0.0001	Significant
A-Temperature	8292.58	8292.58	382.25	0.0001	
B-Sulfuric acid concentration	6029.49	6029.49	277.93	0.0001	
C-hydrolysis time	11,222.50	11,222.50	517.31	0.0001	
AB	60.50	60.50	2.79	0.1259	
AC	256.05	256.05	11.80	0.0064	
BC	518.15	518.15	23.88	0.0006	
A^2	255.36	255.36	11.77	0.0064	
B^2	3999.55	3999.55	184.36	0.0001	
C^2	12,888.95	12,888.95	594.13	0.0001	
Residual	216.94	21.69			Not significant
Lack of fit	101.61	20.32	0.8810	0.5536	

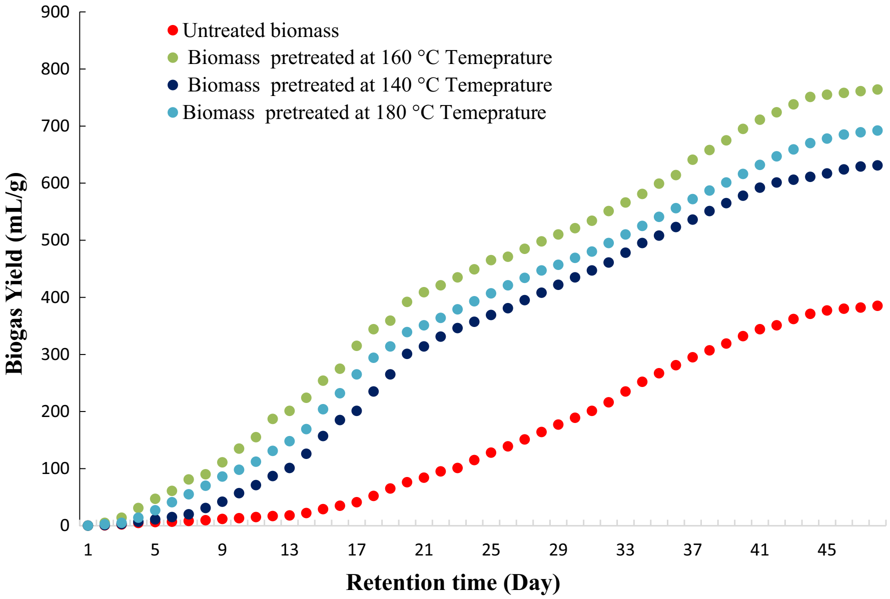

Fig. 5 Effect of Pretreatment temperature (140, 160, and 180 °C) on biogas yield at 3% concentration of H_2SO_4 and 30 min of hydrolysis time

Effects of pretreatment temperature on biogas yield

The three major components of lignocellulose material are cellulose, hemicellulose, and lignin degradation was resulted due to thermochemical pretreatment. The total lignocellulosic fraction of raw wheat straw and coffee husk used in the study were 85.2 and 78.8% as shown in Table 2. From Fig. 5, the temperature has positive effects on the pretreatment of biomass (mixture of wheat straw and coffee husk) to avoid degradability, due to a substantial modification of the substrate. The increment temperature from 140 to 180 °C results that the degradation of complex saccharides (cellulose, lignin, and hemicellulose) to simple saccharides. The simple saccharides such as glucose, xylose, and by-products (acetic acid and formic acid) undergo the pretreatment of lignocellulose biomass. This indicated that from this pretreatment the formation of bio-methane was high. These results reveal that the temperature plays a vital role in the de-polymerization of hemicellulose [23, 33].

As shown in Fig. 5, the first anaerobic digester experiment which treated at different temperatures (140, 160, and 180 °C), at constant sulfuric acid concentration (3%) and cooking time (30 min) vs untreated biomass was compared for biogas production and solids removal. The highest daily biogas production of 61.7 mL/g VS was observed from the biomass treated at 160 °C after 3 days of digestion. The lowest daily biogas production was observed from untreated during the starting days of the digestion as shown in Fig. 5. The rapid biogas production was observed from thermochemical pretreated co-digestion mixtures during the starting days of digestion. This is due to different thermal pretreatment techniques as shown in Fig. 5. The highest cumulative biogas yield from untreated was 385 mL/g VS whereas for pretreated at 140, 160, and 180 °C were 631,764, and 692 mL/g VS. The highest biogas yield of 764 mL/g VS was observed from pretreated at 160 °C. The lowest biogas yield of 385 mL/g VS was obtained from untreated biomass as shown in Fig. 5. Higher biogas yield of 63.89, 98.44, and 79.75% was achieved from pretreatment at 140, 160, and 180 °C as compared to untreated biomass. A higher pretreatment temperature (i.e., 180 °C) corresponded to a higher delignification compared to the milder operative condition (i.e., 150 °C). The lignin removal observed in the pretreated biomass was likely linked to both the cleavage of the bonds between lignin and carbohydrates and the solubilization of lignin.

Effect of sulfuric acid concentration on biogas yield

The other variable that affects the lignocellulose component to give a high amount of cumulative biogas is the percentage of acid concentration hydrolysis of chemo thermal pretreatment. In the second anaerobic digestion, as shown in Fig. 6, the combined effect of co-digestion and thermal pretreatment on the biogas production and solids removal of a pretreated mixture of wheat straw and coffee husk was studied. As shown in Fig. 6, as the H_2SO_4 concentration increased to 3% during pretreatment the cumulative biogas was increased to 724 mL/vs g and decreased when the concentration increased to 4.5%. This attributed increase to the formation of cross-linked aromatic compounds and due to long-time hydrolysis during the pre-treatment activities. The amounts of pseudo-lignin which are formed using high-temperature treatment can be anaerobically degradable [34]. The highest cumulative biogas

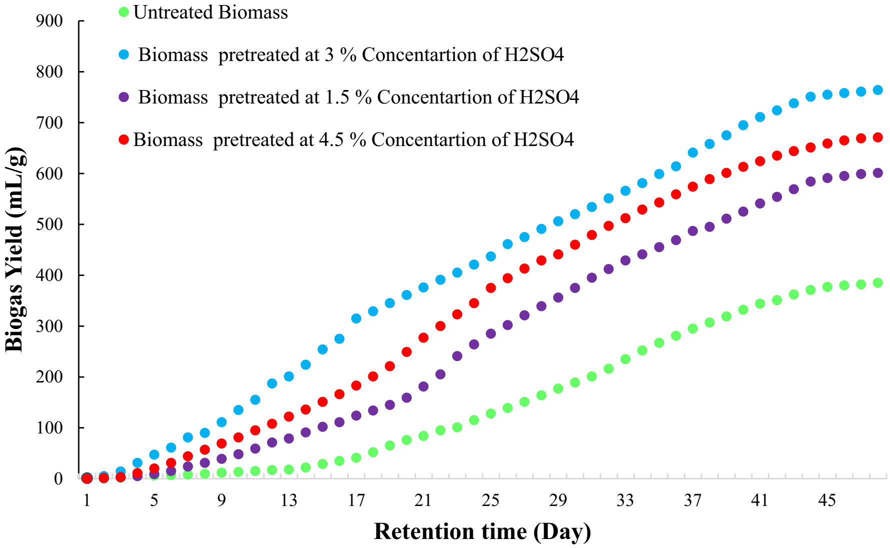

Fig. 6 Effect of Pretreatment concentration of H_2SO_4 (1.5, 3, and 4.5%) on biogas yield at 160 °C of hydrolysis temperature and 30 min of hydrolysis time

yield from untreated was 385 mL/g VS and pretreated at 1.5, 3, and 4.5% were 601, 764, and 671 mL/g VS. The highest biogas yield of 764 mL/g VS was observed from pretreated at 3% and the lowest biogas yield of 385 mL/g VS was obtained from untreated biomass as shown in Fig. 6. Higher biogas yield of 56.10, 98.44, and 74.28% was achieved from pretreatment at 1.5,3 and 4.5% as compared to untreated. Generally, more than 64 percent of biogas was produced from the pretreated mixture of wheat straw and coffee than untreated biomass of the mixture. The dignification of biomass and subsequent glucan-to-glucose conversion was greatly improved by the specified acid pretreatment as compared to the untreated biomass.

Effect of hydrolysis time on biogas yield

In the third anaerobic digestion of the experiment, the hydrolysis time effects on cumulative biogas produced were studied. According to the illustration of Fig. 7, the highest cumulative biogas yield from untreated was 385 mL/g VS and pretreated at 10, 30, and 60 min were 581,764, and 644 mL/g VS. The highest biogas yield of 764 mL/g VS was observed from pretreated at 160 °C. The lowest biogas yield of 385 mL/g VS was obtained from untreated biomass as shown in Fig. 7. Due to its encasing effect, lignin hinders the accessibility of carbohydrates for enzymatic hydrolysis, resulting in low cellulose and hemicellulose degradation and a lower biogas production yield. These improvements were likely related to the partial removal of lignin achieved after the pretreatment. Additionally, it was noted that the accessible surface area for microbial degradation had increased.

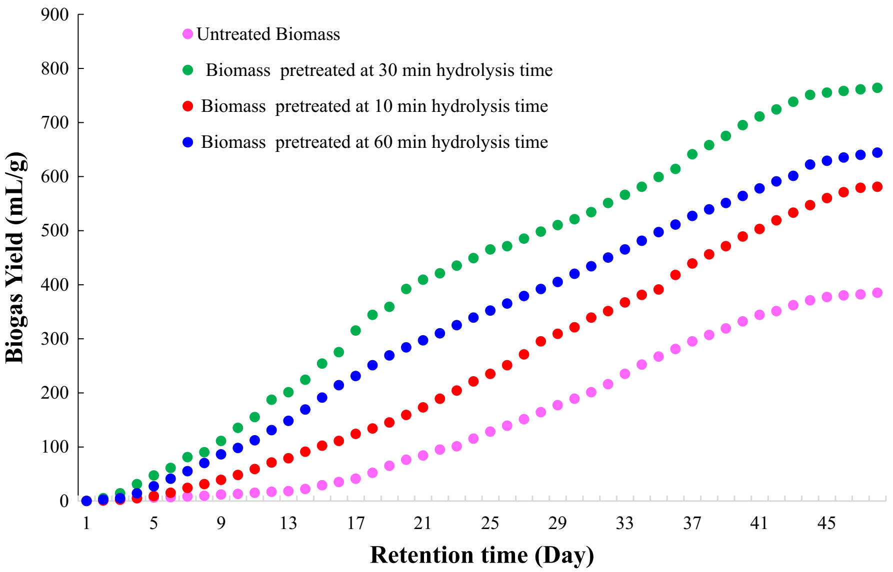

Fig. 7 Effect of hydrolysis time (10, 30, and 60 min) on biogas yield at 160 °C of hydrolysis temperature and 3% H_2SO_4 concentration

Higher biogas yield of 51, 98.44, and 67.3% was achieved from pretreatment at 10, 30, and 60 min as compared to untreated biomass. The increment of biogas was cumulative was obtained when comparing pretreatment to the untreated wheat straw and coffee husk mixture. This is because of hemicellulose degradation and its conversion into simpler molecules like volatile fatty acids and monosaccharides, which might be the cause of the rapid biogas production [32, 35]. In addition to this, the more monosaccharides produced the more methane gas will be produced which is related to rapidly produced biogas. Unusually, as the hydrolysis time increases delignification happens when the ester cross-linking between lignin and xylan is broken due to this cumulative biogas yield increases.

Interaction effects

The response surface curves representing the interaction effects of two variables, i.e., temperature with hydrolysis time and H_2SO_4 concentration with hydrolysis time on the biogas yield were plotted as shown in Fig. 8. Fig. 8a shows that a maximum biogas yield was attained at a high hydrolysis time and considerably middle temperature (160 °C). On the other hand, Fig. 8b shows a maximum biogas yield was obtained at a relatively 160 °C of temperature and at 3% of H_2SO_4 concentration. Almost, no remarkable improvement was observed after longer retention time, high H_2SO_4 concentration, and high temperature. This can explain the decrease of biogas yield, which is well illustrated by the plateau line (red shaded area) after 60 min, 4.5%, and 180 °C of retention time, H_2SO_4 concentration, and temperature.

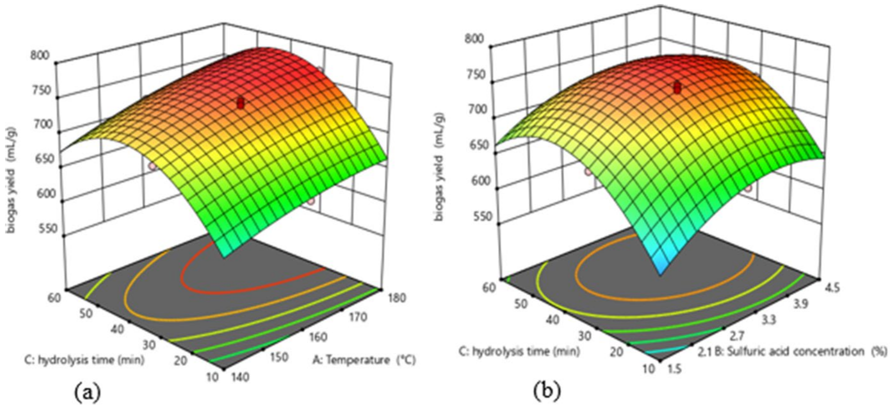

Fig. 8 Interactions effects between **a** hydrolysis time and temperature **b** hydrolysis time and sulfuric acid concentration

Conclusion

The use of lignocellulosic wastes from agricultural and forestry operations as opposed to conventional feedstock (starchy crops) may prove to be an excellent, cost-effective source of sugar for the creation of energy-related purposes. In this study, the effects of thermochemical pretreatment were investigated for the bioaugmentation of biogas from agricultural residues. The increment of biogas cumulative was obtained when pretreated wheat straw was blended with coffee husk as compared to the untreated mixture of its biomass. The maximum cumulative biogas and biomethane obtained from the biomass were 764 mL/g Volatile solid, which was pretreated at 160 °C temperature, 3% concentration of sulfuric acid, and 30 min of cooking time. However, different factors such as substrate and co-substrate composition and quality, environmental factors (temperature, pH, organic loading rate), and pretreatment contribute to the efficiency of the anaerobic digestion process. Therefore, these factors must be optimized to achieve maximum benefit from this technology. This work provides a sustainable solution to the agro-industrial sector to produce biogas energy from wheat straw and coffee husk and enhance its production from their industrial by-products using thermochemical pre-treatment facilities.

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Authors contributions All authors contributed to the conceptualization of the research and writing the manuscript. All authors read and approved the final manuscript.

Data availability The authors declares that the data supporting the findings of this investigation are included in the manuscript.

Declarations

Conflict of interest The authors declare no competing interests.

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