Biomass Conversion and Biorefinery (2021) 11:1395–1406
https://doi.org/10.1007/s13399-021-01340-0

ORIGINAL ARTICLE

Investigation of the effects of different slags as accelerant on anaerobic digestion and methane yield

Ahmet Canan[1] · **Rahman Calhan**[2] · **Mehmet Ozkaymak**[1]

Received: 18 November 2020 / Revised: 27 January 2021 / Accepted: 29 January 2021 / Published online: 17 February 2021

Abstract

In the anaerobic digestion (AD) system, different additives are used to accelerate microorganism activities and increase biogas and methane production. In this study, the effect of different types of slag that emerge in the iron and steel industry on biogas production and methane yield was investigated. Blast furnace slag (BFS), steelmaking converter slag (SCS), and steelmaking ladle slag (SLS) obtained from an integrated iron and steel plant were added to the reactors with cattle manure as substrate at different concentrations (1, 1.5, 2, 2.5, and 3%). In the fed-batch experiments, the highest cumulative biogas yield was 399.5 mL/gVS and the methane yield was 238.2 mL CH_4/gVS in the reactor to which 1% BFS was added. The highest COD removal rates were observed at S1-1, S1-2, S1-5, and S2-2 by 65.36%, 63.88%, 54.08%, and 54.96%, respectively. The biogas production and methane yields were found to be higher in the slag added reactors than in the control reactor, which indicates that slag can be used as an additive in biogas production.

Keywords Anaerobic digestion · Biogas · Renewable energy · Waste · Slag · Methane

1 Introduction

Energy and energy costs, which have a significant impact on the development and economic sustainability of countries, have become even more important today with the rapid development of industrialization and technology, and the demand for fossil fuels as an energy source is increasing substantially. However, conventional energy sources based on fossil fuels are gradually being depleted [1, 2]. With the increasing world population, there is an increase in fossil fuel use in energy production, which results in an increase in the emission of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (NO_2). These gases cause problems such as air pollution and global warming which adversely affect human life [2]. Considering the harm fossil fuels give to the environment, the use of renewable energy sources such as wind, solar, hydroelectric and biogas is becoming widespread as an alternative to the finite resources [3]. Biogas, one of the most widely used alternative energy sources today, emerges as a result of the decomposing of animal, vegetable, domestic, and industrial wastes by microorganisms in an anaerobic (oxygen-free) environment. It is a flammable gas containing a large amount of methane (55–75%) and carbon dioxide (25–45%), and a less amount of ammonia (NH_3), hydrogen sulfur (H_2S), hydrogen (H_2), oxygen (O_2), nitrogen (N_2), and carbon monoxide (CO) [2, 4, 5].

The AD process is a slow process performed by microorganisms and depends on factors such as pH, temperature, hydraulic retention time (HRT), and the C/N ratio. Factors such as low biogas production stability, low biodegradability of the fed substrate, and relatively long biogas production time limit the widespread use of biogas energy production [6, 7]. On the other hand, the ability to produce more biogas per unit of waste allows biogas plants to be operated more economically. Therefore, physical pre-treatments such as grinding, crushing, and shredding, chemical pre-treatments such as acid and alcali addition, and biological pre-treatments such as hydrolysis are applied in order to increase biogas production and methane yield. In addition, organic and inorganic additives that will positively affect the working performance of microorganisms are added to the biogas system. In recent studies, the effects of additives on biogas have been investigated intensively [8, 9].

✉ Ahmet Canan
ahmetcanan@karabuk.edu.tr

[1] Faculty of Technology, Department of Energy Systems Engineering, Karabuk University, Karabuk, Turkey

[2] Faculty of Engineering, Department of Environmental Engineering, Karabuk University, Karabuk, Turkey

Additives added to the biogas system increase the localized surface area and provide the desired conditions for microorganisms to be adsorbed to the substrate. In this way, the activity of enzymes and microorganisms is accelerated, the degradation time of the substrate is shortened, and the biogas production potential and methane yield can be increased through a higher amount of organic matter degradation as a result of the appropriate decomposition conditions [7, 10].

Studies conducted so far have used inorganics including micro (Fe, Mn, Mo, W, Se, Co, Ni, Cu, Zn, Mg, and Ca) and macronutrients (P, N, and S) as additives. Studies have shown that micro and macronutrients added in certain proportions prevent the accumulation of volatile fatty acids or stabilize the pH at optimum values by ensuring the minimum alkaline level. In this way, both biogas production stability and methane production increase [11–14]. Zhang et al. [14] studied a combination of Fe, Co, Mo and Ni trace metal elements and reported that increased biogas and methane yield 35.5% and 504 mL/gVS, respectively. Furthermore, Facchin et al. [15] added Co, Mo, Ni, Se, and W metal mixture into the AD system and achieved increased methane production in a range of 45–65% in low metal concentrations. Janke et al. [16] investigated effects of macronutrient supplementation (S, N, and P) of N alone or in combination with S and P and observed a significant increment of specific methane production by 17% and 44%, respectively. Besides, macronutrient rich additives can be used to improve biogas and methane yield. Xu et al. [17] used phosphorus rich vermiculate as accelerant in batch AD system which increased biogas production (39.38%).

Enzymes and microorganisms also can be used as organic additives to the AD system since enzymes can help degrade macromolecules to soluble micro molecules [18]. Weide et al. [19] reported that the main effect of addition enzyme to the AD system concluded with accelerated degradation of substrates besides that accelerated methane and biogas production. Many researchers reported that adding metal oxides, minerals, transition metal compounds and carbon materials to the AD system can improve biogas production and methane yield [10, 20]. Zhang et al. [21] indicated that addition of niobium-based oxides to the AD system resulted with higher cumulative biogas production (437.1–522.7 mL/g VS) and chemical oxygen demand rates (56.08–65.19%). Yun et al. [20] reached higher biogas production (565.01–617.85 mL/g VS), chemical oxygen demand degradation rate (67.17–70.45%), total solids, and volatile solids reduction rates (29.76–34.71%, 51.83–60.88%) when added transition metal oxide accelerants to the AD system. Chen et al. [22] showed that using biomass-derived carbon-based composites, acts as an electron carrier in the electron transfer system thus accelerate electron transfer between acetogen and methanogen microorganisms and so, this improves the TCOD degradation rate, TS and VS reduction, and biogas yield in the AD system.

Different types of materials used in iron and steel production produce many different wastes. Failure to properly dispose of these wastes can lead to serious environmental problems. Slag waste is one of the most produced wastes in iron and steel industry. Since slags are produced in large quantities as a result of pyrometallurgical processes, they are large sources of waste if not recycled properly. As a result of rapid industrialization, there is an increasing need for storage areas to conserve the metallurgical slags, which increases the costs. These areas where waste materials are stored pollute air, water, and soil, which have an important place in human life [23].

Today, slag wastes can be used for various purposes. According to the source they emerge, slags can be used in material production within the plant, road construction, cement and concrete production, fertilizer production, and soil reclamation [24]. In addition, slag has the potential to be used as an additive in anaerobic biogas production due to the FeO, CaO, SiO_2, MgO, Al_2O_3, and MnO compounds it contains and its ability to provide the micro-elements required for the microorganisms during anaerobic degradation [25]. The number of studies on biogas production with slag wastes is limited in the literature. More studies are needed on slag wastes, which have the potential to be used as additives in biogas production. In spite of different additives also including steel slag have been used to improve the biogas efficiency but BFS has not been used and not compared with other slags as accelerant. The aim of this study can be summarized as follows: (i) characterizing different slags (BFS, SCS, and SLS) occurring from an integrated iron and steel facility to use as additives in biogas production, (ii) comparing and investigating of effects of these slags on biogas production and methane yield (iii) determining of optimum slag concentration to use as additives.

2 Material and method

2.1 Characterization of cattle manure

The fresh cattle manure used in the experiments was obtained from a local animal breeding farm. Analyses were performed on the manure samples to determine its characteristics. The characteristics of the cattle manure used are given in Table 1. The inoculum used in the experiments was taken from the biogas system with 40 L volume in the Environmental Engineering Laboratory. In the laboratory scale biogas system, a mixture of cattle manure and poultry manure is used to produce biogas. The characteristics of the inoculum are given in Table 1.

Table 1 Characteristics of cattle manure and inoculum

	Cattle manure	Inoculum
C (%)	43.51	36.2
N (%)	6.12	4.21
C/N	7.1	8.61
Total solids (TS (%))	23.75	12.53
Volatile solids (VS (%))	86.72	91.47
VFA (mg/L))	58,300	-
Total nitrogen (mg/L))	13,300	-
Chemical oxygen demand (COD (mg/L))	45,310	28,251

2.2 Slag Sample Characterization

The slags added in the experiments were obtained from an integrated iron and steel production plant. Three different slags are produced in the plant, which are BFS, SCS, and SLS. The slags were dried in the oven for 24 h at 103–105 °C before their use in the biogas system. Since the particle size of the slags was between 0.2 and 0.5 mm, no extra grinding process was required.

2.3 Leaching test

European batch leaching test EN 12457-2 [26] was administered to determine the substances that can leak from the slag samples to be used. The particle sizes of the slags used were between 0.05 and 4 mm, and deionized water was used as the solvent. In the batch leaching test, each slag sample was tested three times. Five grams of slag sample was added to each leach bottle, and then, deionized water was added so that the liquid to solid ratio (L/S) was 20. The samples which were shaken at 200 rpm agitation speed for 24 h were analyzed by filtering through a filter with 0.45 μm pore diameter at the end of 24 h.

2.4 Experimental setup

All the experiments were carried out in 1-liter glass reactors at 600 mL working volume. The reactors were sealed using pneumatic equipment. The impermeability of the reactors was tested manually using a hand pump (Fig. 1). In the experiments, a total of 48 reactors were operated (3 for the control reactor, 15 for the BFS, 15 for the SCS, and 15 for the SLS). Cattle manure was used as the main substrate in all reactors, and the concentration of the additives was 1, 1.5, 2, 2.5, and 3% by weight (Table 2). One hundred milliliter of inoculum was added to all the reactors and the dry matter ratio in the reactor was adjusted to be 7%. All the experiments were repeated three times for each additive concentration. Water baths were used to provide the necessary temperature for AD, and all the reactors were operated under mesophilic conditions (36 ± 1 °C) for 60 days. The reactors were manually shaken every day so that the environment in the reactor was completely mixed.

2.5 Analytical methods

The amount of biogas generated in the reactors was measured daily based on the water displacement principle. The CH_4, CO_2, H_2S and O_2 contents of the biogas obtained were measured daily with a biogas analyzer (GEOTECH 5000, UK). The C, N, COD, TS and VS contents of the substrate were carried out following the standard methods [27]. The chemical analyses of the slags used as additives were conducted with X-ray diffraction spectrometer (XRF) (Rigaku Ultima IV, Japan). The pH values of the reactors at the first day of feeding and at the end of 60 days were measured with a WTW720i pH meter. Characterization of particle size and shape of powder slag samples was observed using a scanning electron microscope (SEM) (Carl Zeiss, Ultra Plus Gemini, FESEM, Germany). The chemical analysis of leachate of slags was observed by inductively coupled plasma–mass spectrometer (IPC-MS) (Thermo Scientific, X SERIES 2, USA). The slags used in the experiments were dried at 103–105 °C for 1 day before use.

3 Results and discussions

3.1 Structural characteristics of slags

Three different types of slag were used in the study, namely BFS (S1), SCS (S2), and SLS (S3) produced in an integrated

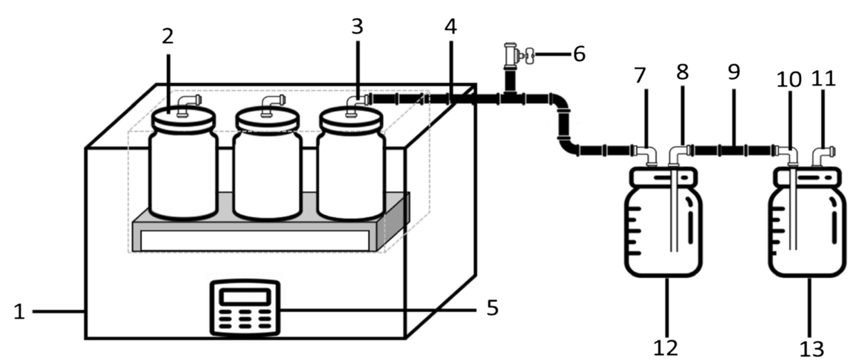

Fig. 1 Experimental setup, 1. Temperature controlled water bath, 2. Digester, 3. Biogas outlet, 4. Biogas tube 5. Control panel, 6. Biogas sample point, 7. Biogas inlet, 8. Water outlet, 9. Water tube, 10. Water inlet, 11. Air pipe, 12. Biogas collecting bottle, 13. Water collecting bottle

Table 2 Concentrations of slags added to the reactors

Reactor	S1-1	S1-2	S1-3	S1-4	S1-5	S2-1	S2-2	S2-3	S2-4	S2-5	S3-1	S3-2	S3-v3	S3-4	S3-5	Control
Concentration (%w/w)	1.0	1.5	2.0	2.5	3.0	1.0	1.5	2.0	2.5	3.0	1.0	1.5	2.0	2.5	3.0	0.0

iron and steel production plant. The chemical compositions of the slags are given in Table 3. Slag is a by-product of iron and steel production. It has high porosity, large surface area and good hydraulic conductivity, and contains Fe_2O_3, CaO, SiO_2, Al_2O_3, MgO, MnO, Cr_2O_3, and some small metal oxide components [28]. The basicity index of the slags was calculated using the formula of (CaO + MgO) / (SiO_2 + Al_2O_3), and it was calculated as 0.76 for the BFS, 2.10 for the SCS, and 3.95 for the SLS. The basicity index has important effects on the leaching of slags due to the dissolution and hydrolysis of basic oxides compared to soluble acidic oxide [29].

BFS is produced during the production of crude liquid iron from the ore and is separated from the crude liquid iron during the casting process after production. The main components of BFS are Al_2O_3 (11.99%), CaO (28.81%), SiO_2 (37.54%), and MgO (8.94%).

SCS is produced after the addition of various flux materials (calcite, dolomite) to the liquid material in order to remove the impurities resulting from the interaction of the scrap material and the liquid crude iron from the blast furnace. The formation of the resulting steel slag, the technique used in production, the Si content of the raw material used, and the amount of lime used affect the chemical and mineral composition and the amount of slag produced [30]. The main components of the SCS are Fe_2O_3 (54.87%), CaO (18.12%), SiO_2 (10.84%), and MgO (9.76%). Due to the high Fe_2O_3 content it has, SCS can be reused in iron and steel production.

SLS is produced after the converter slag is produced when the scrap material and the liquid crude iron are melted, with the removal of the unwanted impurities by adding flux materials into the liquid crude iron in order to produce the desired steel. The main components of the SLS are CaO (51.53%), Fe_2O_3 (19.74%), SiO_2 (13.47%), and MgO (8.11%). Due to the low levels of Fe_2O_3 it contains, the rate of reusing the ladle slag is very low.

SEM analysis was performed to examine the surface morphology and structure of the slags used in the study. BFS is tapped out of the furnace at high temperature (1400–1500 °C) nearly liquid iron temperature and separated from liquid iron at the slag skimmer where slag is drained away by channels to the granulation pool. In the granulation pool, the slag is cooled by water, during this cooling round pores are formed in the slag and has a smooth surface and sharp edges as seen in Fig. 2a. EDX results showed that BFS is mainly composed of O, Si, Ca and Fe elements (Fig. 2b).

SEM analysis and EDX results of steel making converter slag and SLS in Fig. 2c and Fig. 2e, respectively. Figures show that slags are composed of irregular particles of different sizes. Small particles are piled up irregularly. There are tiny pores on each particle. This morphological structure may provide the required surface area for microorganisms to adsorb on the slag. EDX results of steel making converter slag and ladle slag showed that mainly O, Ca, C, Si, and Fe elements were present on the surface (Fig. 2d, f). It was determined that while O, Ca and C ratios were close to each other in both slags, Fe ratio was higher in steel making converter slag and Si ratio was higher in steel making ladle slag.

Table 3 The chemical composition of blast furnace and steelmaking slags (%)

Slags	BFS (slag 1)	SCS (slag 2)	SLS (slag 3)
Al_2O_3 (%)	11.99	2.43	1.6
CaO (%)	28.81	18.12	51.53
MgO (%)	8.94	9.76	8.11
MnO (%)	2.11	2.39	3.92
S (%)	0.49	0.23	0.12
Fe (%)	0.63	-	-
K_2O (%)	0.73	0.26	0.05
Na_2O (%)	0.14	0.04	0.04
TiO_2 (%)	1.53	0.32	0.41
SiO_2 (%)	37.54	10.84	13.47
Fe_2O_3 (%)	-	54.87	19.74
P_2O_5 (%)	-	0.1	1.01
Diğer (%)	7.09	0.64	-

3.2)Leaching test results

The leaching test of the BFS (Table 4) showed that the main substances that can pass from the slag to water are Ca, Na, Mg, Al, Fe, and K. The most abundant substance in water was Ca with 338.412 mg/kg, followed by Na with 114.057 mg/kg and Al, Mg, and Fe with approximately 30 mg/kg.

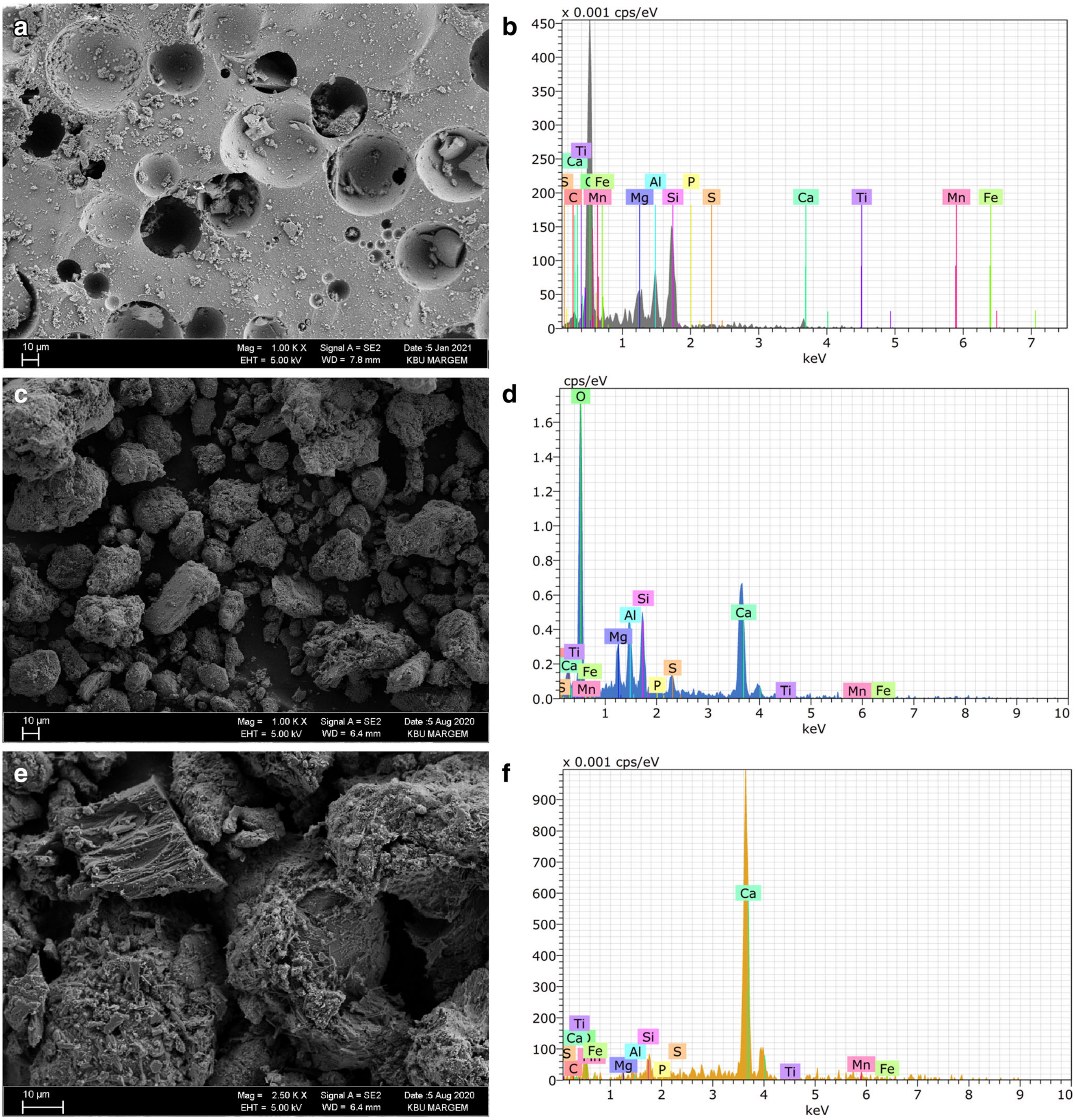

Fig. 2 (a) SEM image of BFS, (b) EDX result of BFS, (c) SEM image of SCS, (d) EDX result of SCS, (e) SEM image of SLS, (f) EDX result of SLS

According to the leaching test of the SCS, the most abundant substance in water was Na with 867.779 mg/kg, followed by Ca with 638.485 mg/kg. The amount of Al, Mg, and Fe, which was around 30 mg/kg in BFS, was found to be fairly low.

The leaching tests revealed that of all the slags, the highest amount of Ca (742.366 mg/kg) was found in the SLS. Na was found to be less with 585.292 mg/kg, compared to the blast furnace converter slag.

Ca, Mg, Na, K, and Fe are the macronutrients necessary for the growth and reproduction of microorganisms. Fe plays a major role in cellular respiration as an important component of cytochromes and iron-sulfur proteins

Table 4 Leaching test results

Slag	Ca (mg/kg)	Si (mg/kg)	Al (mg/kg)	Mg (mg/kg)	K (mg/kg)	Fe (mg/kg)	Ti (mg/kg)	Na (mg/kg)	Mn (mg/kg)	P (mg/kg)
BFS	338.412	2.38	30.789	39.033	13.673	30.149	1.899	114.057	3.840	0.869
SCS	638.485	0.343	2.175	3.798	89.423	3.488	0.068	867.779	2.464	0.623
SLS	742.366	0.283	2.139	0.788	114.968	0.496	0.088	585.292	0.388	0.544

involved in electron transport. K and Mg macronutrients play a role in the activity of many enzymes, while Ca helps to strengthen the cell wall [31]. It is seen that there are different proportions of macronutrients in the

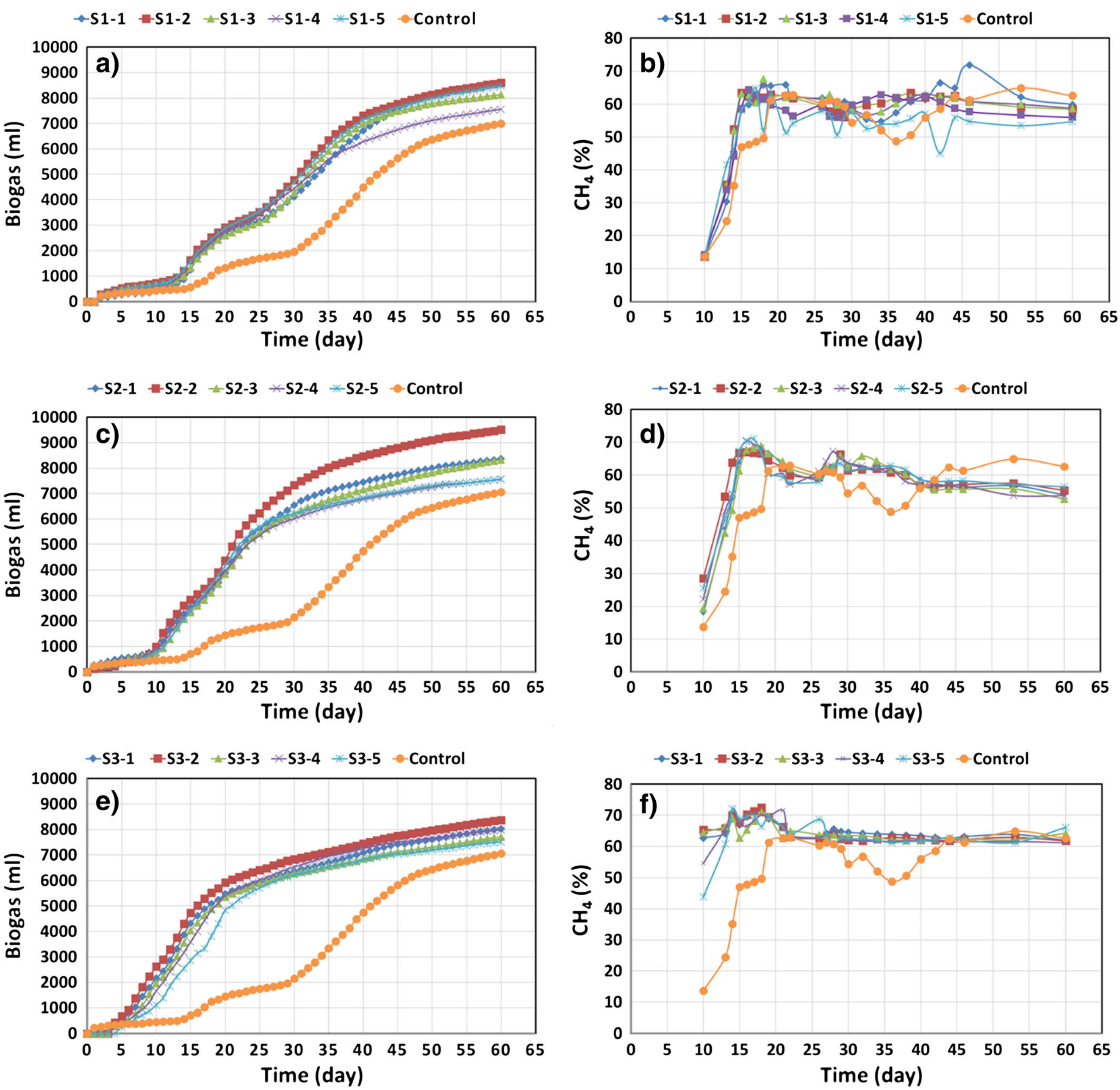

Fig. 3 Daily (a, c, e) and cumulative (b, d, f) biogas production of the reactors to which different concentrations of slag were added

composition of the slags used in the experiments. The macronutrients in the composition of the slags contribute to the anaerobic degradation process by supporting microbial growth and development.

3.3 Performance of AD with slags

3.3.1 The effect of slag types on methane yields from AD

As mentioned above, three different slag types obtained from an integrated iron and steel production facility were used in the study. Slags were added to the reactors as additives at the rates specified in Table 2, and their effects on biogas production and methane yield were examined. The methane yields of the slags are given in Fig. 3. As seen in the figure, the highest cumulative biogas production was in reactor S2-2 with 9512.7 mL, while the highest biogas yield was in reactor S1-1 with 399.46 mL/gVS. In their study with magnetite, which also including substances found in slag, Liu et al. [32] obtained a biogas yield of 227.62 mL/gVS. On the other hand, Shen et al. [33] obtained a biogas yield of 319.44 mL/gVS in their study with the biochar. Based on these results, it can be said that different elements in the slag content affect the biogas yield.

In the AD process, when there are slowly degrading substances, the speed limiting phase is the hydrolysis phase in which substances with large structures are converted into substances with smaller structures [34]. The rapid completion of the hydrolysis phase also enables the rapid realization of the following phases, which are the acetogenesis and methanogenesis phases. As can be seen in Fig. 3, the hydrolysis phase was completed faster in all reactors with additives compared to the control reactor. Han et al. [35] stated that the CaO and MgO contents create a strong alkaline buffer environment in the anaerobic degradation system, which increases the cumulative biogas production. In our study, the CaO and MgO contents were determined as 28.81 and 8.94 wt%, 18.12 and 9.76 wt%, and 51.53 and 8.11 wt% for S1, S2 and S3, respectively. When the pH values at the beginning and end of the experiment given in Table 5 are examined, it can be said that CaO and MgO contribute to the alkalinity of the environment. However, contrary to Han et al.'s study [35], higher cumulative biogas production was not observed in slags with high CaO and MgO content.

When Fig. 4 is examined, it is seen that in all reactors, cumulative biogas production is higher compared to the control reactor. However, biogas efficiency was lower in S2-4, S2-5, S3-2, and S3-5 reactors than the control reactor with a biogas yield of 293.74 mL/gVS. It is seen that slags added as additives in all other reactors increased biogas yield by 2–26%. BFS was the additive that increased biogas yield most with 35.9%, while the SCS and SLS made a 28.9% and 23.8% contribution to biogas yield, respectively.

Table 5 Biogas yields, total biogas production, and methane yields of different slags

Reactor	pH (initial)	pH (final)	Biogas yield (mL/gVS)	Total biogas production (60 days) (mL)	CH_4 content (%)	CH_4 yield (mL/gVS)
S1-1	7.89 ± 0.05	7.14 ± 0.02	399.46 ± 51.5	8609.4 ± 581	59.62 ± 5.3	238.2 ± 18.5
S1-2	7.78 ± 0.07	7.03 ± 0.04	377.77 ± 21.9	8651.3 ± 547	58.68 ± 1.7	221.7 ± 22.7
S1-3	7.75 ± 0.12	7.01 ± 0.01	328.65 ± 33.4	8193.2 ± 329	59.41 ± 2.6	195.25 ± 19.4
S1-4	7.34 ± 0.09	6.98 ± 0.02	321.84 ± 19	7627.7 ± 447	58.65 ± 4.8	188.77 ± 31.5
S1-5	7.46 ± 0.11	6.99 ± 0.06	360.91 ± 20.8	8523 ± 542	55.1 ± 3.2	198.95 ± 12.3
S2-1	7.74 ± 0.01	7.09 ± 0.01	346.04 ± 32.5	8373.8 ± 196	59.29 ± 1.9	205.19 ± 23.4
S2-2	7.76 ± 0.06	7.1 ± 0.03	378.91 ± 57.5	9512.6 ± 581	60.32 ± 2.4	228.59 ± 16.3
S2-3	7.81 ± 0.03	7.09 ± 0.04	336.59 ± 47.7	8330.6 ± 600	58.99 ± 2.1	198.57 ± 11.8
S2-4	7.91 ± 0.08	7.13 ± 0.02	287.01 ± 4.5	7570.1 ± 91	59.97 ± 1.8	172.13 ± 17.3
S2-5	7.78 ± 0.18	7.08 ± 0.01	249.46 ± 54.3	7572.7 ± 644	60.55 ± 3.6	151.05 ± 12.8
S3-1	7.83 ± 0.15	6.69 ± 0.05	363.80 ± 17.5	8020.4 ± 384	64.08 ± 4.1	233.15 ± 26.4
S3-2	7.79 ± 0.06	6.65 ± 0.02	277.67 ± 55.6	8369.9 ± 326	64.54 ± 2.4	179.21 ± 23.9
S3-3	7.84 ± 0.20	6.65 ± 0.02	301.13 ± 72.6	7710.1 ± 977	62.98 ± 3.5	189.66 ± 12.7
S3-4	7.99 ± 0.23	6.67 ± 0.05	313.25 ± 20.7	7981.1 ± 526	64.05 ± 2.7	200.65 ± 18.8
S3-5	8.24 ± 0.01	6.66 ± 0.03	239.66 ± 59.8	7502 ± 290	62.85 ± 1.8	150.63 ± 16.4
Control	7.07 ± 0.07	6.49 ± 0.07	293.74 ± 63.6	7064.8 ± 744	55.99 ± 2.1	164.48 ± 16.1

Average methane yields obtained from the reactors are given in Table 5. In all the reactors where the experiment was carried out, methane peak values were reached earlier compared to the control reactor. According to daily methane production data, peak methane production (64.9%) was reached on the 22nd day in the control reactor, while the peak values were reached on the 14th day in S3-4 (72%) and S3-5 (72%) reactors. It was observed that peak values were reached on the 18th day at the latest in all the reactors to which slags were added. When Table 5 is examined, the highest methane yield was reached in S1-1 with 238.20 mL/gVS, followed by S3-1 with 233.15 mL/gVS and S2-2 with 228.60 mL/gVS. The methane yield of the control reactor was 164.48 mL/gVS, which is approximately 31% lower compared to S1-1 with the highest methane yield.

3.3.2 The effect of slag dose on methane yields from AD

In addition to the type of slag, the effect of different amounts of slag on biogas production and methane yield was also investigated in the study. For this purpose, each slag type was added in the proportions of 1, 1.5, 2, 2.5, and 3% by weight, respectively. As shown in Fig. 4, the biogas and methane yield decreased depending on the increasing slag ratio in the reactors with BFS; however, it was observed that both the methane yield and the biogas yield increased in the reactor where 3% BFS was added, compared to the reactors to which 2% and 2.5% of slag was added. It was observed that biogas and methane yield increased in all reactors compared to the reference control reactor. In the reactors where BFS was added, the highest methane yield and the highest biogas yield were achieved in the reactor where 1% of slag was added with 238.20 $mLCH_4$/gVS and 399.5 mL/gVS, respectively. Fe is an essential element in AD system by virtue of improving microbial enzymatic activities [36]. Furthermore, Fe acts as electron acceptor by microorganisms in the AD system, which positively affects the DIET performance of microorganisms [37, 38]. Yun et al. [39] investigated the effect of iron salts in the AD system and found that the addition of $Fe(NO_3)_3$ and optimized organic composite additive (OOCA) increased the biogas yield by 34.51%. As can be seen in Table 4, BFS releases much more Fe in the aquatic environment compared to the other slags. Therefore, it is thought that higher biogas production is obtained in reactors where BFS with higher Fe content.

It was observed that in the reactors where 1, 1.5, and 2% of SCS was added, both methane and biogas yields increased compared to the reference control reactor; however, in the reactors to which 2.5% and 3% of slag was added, both the biogas and methane yields decreased compared to the control reactor. The highest biogas and methane yields were achieved in the S2-2 reactor where 1.5% of slag was added, with 378.9 mL/gVS and 228.59 mL CH_4/gVS, respectively. It was observed that biogas and methane yields decreased with increasing amounts of slag. It can be said that the amount of slag added in reactors S2-4 and S2-5 negatively affected the vital activities of microorganisms and created an inhibition effect.

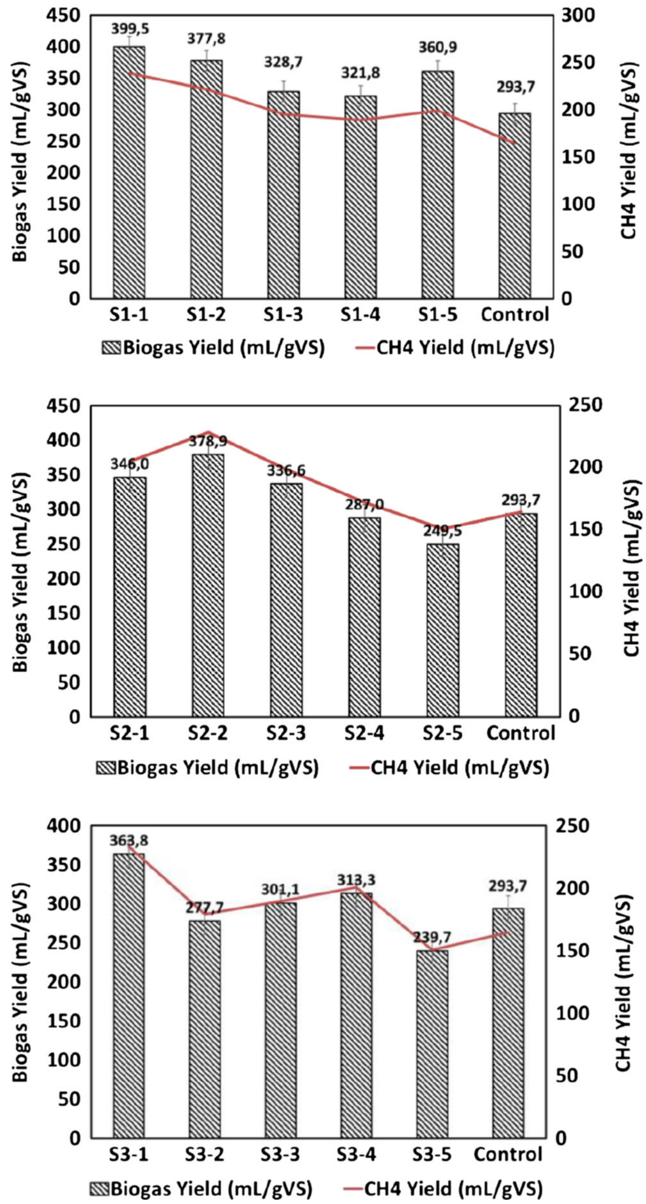

Fig. 4 Biogas and methane yield of reactors to which different concentrations of slag were added

In the reactors with SLS, the highest methane and biogas yields were obtained in reactor S3-1, where 1% of slag was added, with 233.15 mL CH_4/gVS and 363.81

Table 6 Relevant results of literature on using different additives

Additives[a]	Substrates[a]	Concentration	HRT	Temperature	Biogas yield	Effect on AD process	Reference
SS	COM	1 wt%	35 days	36 ± 1 °C	594 mL/g VS	Increased 64.0%[b]	[35]
Zeolite	SM, CM, WS	1 g	30 days	35 °C	218.41 L/kg VS	Increased 51.01%[b]	[32]
Magnetite	SM, CM, WS	3 g	30 days	35 °C	227.62 L/kg VS	Increased 52.01%[b]	
Magnetite	PM, WS	3 g	51 days	35 °C	195 mL/g TS	Increased 72.1%[b]	[41]
Magnetite	WAS	27 g/L	56 days	37 ± 1 °C		Increased 7.3%[c]	[42]
GAC	WAS	27 g/L	56 days	37 ± 1 °C		Increased 13.1%[c]	
Vermiculite	APW, DM	0.3 wt%	35 days	36 ± 1 °C	353.96 mL/g VS	Increased 51.21%[b]	[17]
NM	PS	50 mg/L	10 days	35 °C	146 mL/g VS	Increased 7.5%[c]	[43]
GP	PS	500 mg/L	10 days	35 °C	151 mL/g VS	Increased 11.2%[c]	
AC	PS	15 g/L	10 days	35 °C	152 mL/g VS	Increased 11.8%[c]	
BFS	CM	1 wt%	60 days	36 ± 1 °C	399.46 mL/g VS	Increased 35.9%[b]	This study
SCS	CM	2 wt%	60 days	36 ± 1 °C	378.91 mL/g VS	Increased 28.9%[b]	
SLS	CM	1 wt%	60 days	36 ± 1 °C	363.80 mL/g VS	Increased 23.8%[b]	

[a] SS, steel slag; COM, cow manure; SM, sheep manure; CM, chicken manure; WS, wheat straw; PM, pig manure; WAS, waste activated sludge; GAC, granular activated carbon; APW, aloe peel waste; DM, dairy manure; NM, nano magnetite; PS, primary sludge; GP, graphite powder; AC, activated carbon

[b] Increase in biogas yield

[c] Increase in methane yield

mL/gVS, respectively. While the biogas yield was lower in the reactors where 1.5% and 3% of slag was added compared to the control reactor, the methane yield was higher in the reactor to which 1.5% of slag was added. As a result, the study revealed that low concentrations are more suitable for each slag to be used as an additive. The addition of 1% of BFS increased biogas yield by about 26% and methane yield by 31%, while the addition of 1.5% of SCS increased biogas yield by 22% and methane yield by 28%, and the addition of 1% of SLS increased

Table 7 Initial and final TS, VS, and COD concentrations and reduction rates

Reactors	TS and VS						COD		
	Initial TS (g)	Final TS (g)	TS reduction (%)	Initial VS (g)	Final VS (g)	VS reduction (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
S1-1	24.13 ± 0.13	11.57 ± 0.12	52.05 ± 0.45	20.38 ± 0.22	11.98 ± 0.15	41.22 ± 0.21	53,000 ± 359.5	18,358 ± 320.5	65.36 ± 0.45
S1-2	27.28 ± 0.17	14.88 ± 0.23	45.45 ± 0.34	23.01 ± 0.31	14.84 ± 0.21	35.51 ± 0.34	55,022 ± 245.5	19,875 ± 267.5	63.88 ± 0.36
S1-3	27.72 ± 0.12	18.58 ± 0.32	32.97 ± 0.28	23.54 ± 0.18	15.31 ± 0.14	34.97 ± 0.45	50,167 ± 190.7	26,930 ± 190.7	46.32 ± 0.29
S1-4	28.08 ± 0.21	17.46 ± 0.10	37.82 ± 0.19	23.84 ± 0.25	15.47 ± 0.34	35.10 ± 0.22	50,167 ± 365.4	34,136 ± 345.4	31.96 ± 0.37
S1-5	28.36 ± 0.23	14.82 ± 0.22	47.74 ± 0.24	23.75 ± 0.33	14.55 ± 0.32	38.73 ± 0.34	59,473 ± 289.5	27,309 ± 275.3	54.08 ± 0.22
S2-1	27.71 ± 0.10	15.18 ± 0.27	45.22 ± 0.36	22.64 ± 0.42	14.62 ± 0.25	35.42 ± 0.52	47,335 ± 190.8	28,371 ± 230.6	40.06 ± 0.33
S2-2	27.96 ± 0.12	16.78 ± 0.13	39.99 ± 0.16	23.13 ± 0.24	14.21 ± 0.19	38.56 ± 0.36	43,113 ± 220.3	19,420 ± 165.8	54.96 ± 0.48
S2-3	28.32 ± 0.12	14.86 ± 0.12	47.53 ± 0.29	23.42 ± 0.22	15.11 ± 0.43	35.47 ± 0.26	40,862 ± 319.5	24,093 ± 183.9	41.04 ± 0.27
S2-4	31.74 ± 0.34	16.44 ± 0.23	48.20 ± 0.32	26.48 ± 0.31	17.88 ± 0.26	32.47 ± 0.24	44,922 ± 288.5	29,281 ± 254.8	34.82 ± 0.56
S2-5	32.28 ± 0.25	22.66 ± 0.38	29.80 ± 0.27	27.05 ± 0.18	19.83 ± 0.22	26.69 ± 0.40	48,145 ± 193.7	33,518 ± 320.7	30.38 ± 0.35
S3-1	27.42 ± 0.23	15.28 ± 0.25	44.27 ± 0.25	22.05 ± 0.27	14.29 ± 0.37	35.18 ± 0.23	50,167 ± 345.8	24,578 ± 154.8	51.01 ± 0.57
S3-2	27.84 ± 0.15	19.38 ± 0.20	30.39 ± 0.18	22.69 ± 0.45	17.64 ± 0.35	22.26 ± 0.19	46,931 ± 157.5	25,489 ± 165.7	45.69 ± 0.23
S3-3	28.38 ± 0.18	17.46 ± 0.15	38.48 ± 0.30	23.24 ± 0.39	16.27 ± 0.26	30.00 ± 0.22	43,694 ± 267.4	27,613 ± 144.6	36.81 ± 0.18
S3-4	30.66 ± 0.16	18.72 ± 0.17	38.94 ± 0.21	25.48 ± 0.41	17.31 ± 0.28	32.06 ± 0.29	51,786 ± 250.3	28,675 ± 215.6	44.63 ± 0.34
S3-5	31.02 ± 0.12	20.44 ± 0.19	34.11 ± 0.22	26.03 ± 0.22	22.18 ± 0.33	14.78 ± 0.25	46,122 ± 187.5	30,950 ± 273.8	32.89 ± 0.27
Control	28.54 ± 0.22	18.48 ± 0.24	35.25 ± 0.34	24.20 ± 0.33	18.23 ± 0.42	24.68 ± 0.15	52,393 ± 310.6	28,978 ± 310.5	44.69 ± 0.20

biogas yield by 19% and methane yield by 29%. According to leaching result of the slags Ca contents of steelmaking slag groups were observed higher than BFS. Some researchers reported that Ca ions were essential in polysaccharide production as cofactors. Besides, at high concentrations of Ca ions can inhibited the methane production and shows growth-inhibition effect in AD systems [40]. Hence, it can be said that biogas yields decrease with increasing slag concentrations in reactors to which steelmaking slag groups are added.

In order to compare the effects of different additives on the AD system, a summary of the results of the different studies is given in Table 6. Different additives have been used in the AD system at different doses and under different conditions, and it has been observed that when added in appropriate doses, they can increase biogas production and methane yield. In this study adding different slags increased biogas yield 23.8–35.9%.

3.3.3 VS, TS, and COD removal efficiencies

TS, VS, and COD removal rates are the most important indicators for biodegradability of substrate [44]. TS, VS and COD removal rates were given in Table 7. TS reduction rates for S1, S2, and S3 range between 32.97–52.05%, 29.80–48.20%, and 30.39–44.27%, respectively where the highest TS reduction rate was observed in S1-1 (52.05%). However, VS reductions were 35.10–41.22%, 26.69–38.56%, and 14.78–35.18% respectively where the highest VS reduction rate was observed in S1-1 (41.22%). Figure 5 shows initial and final COD and COD removal rates of reactors. When compared to the control highest COD removal rates were observed at S1-1, S1-2, S1-5, and S2-2 by 65.36%, 63.88%, 54.08%, and 54.96%, respectively. As can be seen in Table 6 adding BFS to the AD system dramatically effect COD removal rates. Zhang et al. [45] obtained similar COD removal rates (46.8–69.1%) in which they examined the effects of low-cost composite accelerants on anaerobic degradation.

Overall, when compared to the control, using slag additives enhances TS, VS reduction, and COD removal rates so it can be said that adding slag to the AD system in certain proportions healed the environment for anaerobic microorganisms in AD.

4 Conclusions

Our study revealed that different slag types can be used as additives in biogas production. When 1% of BFS was added, the total cumulative biogas yield and biogas production yield were found to be 399.5 mL/gVS. On the other hand, when 1.5% of SCS and 1% of SLS were added, the total cumulative biogas yield and biogas production yield were found to be 378.9 mL/gVS and 363.8 mL/gVS, respectively. As far as methane yields are concerned, when 1% of BFS was added, the yield was 238.2 mL CH_4/gVS. On the other hand, when 1.5% of SCS and 1% of SLS were added, the methane yield was 228.59 mL CH_4/gVS and 233.15 mL CH_4/gVS, respectively. The results show that in addition to increasing biogas and methane yield, slags accelerate the hydrolysis phase, which is the first stage of decomposition of organic substances and meet the alkalinity requirement in the biogas system. The study was carried out with batch feeding, and the slags used do not completely dissolve in biogas. Therefore, there is a certain amount of slag in the waste material generated after biogas production, and the resulting waste material has the potential to be used as fertilizer, which requires further studies.

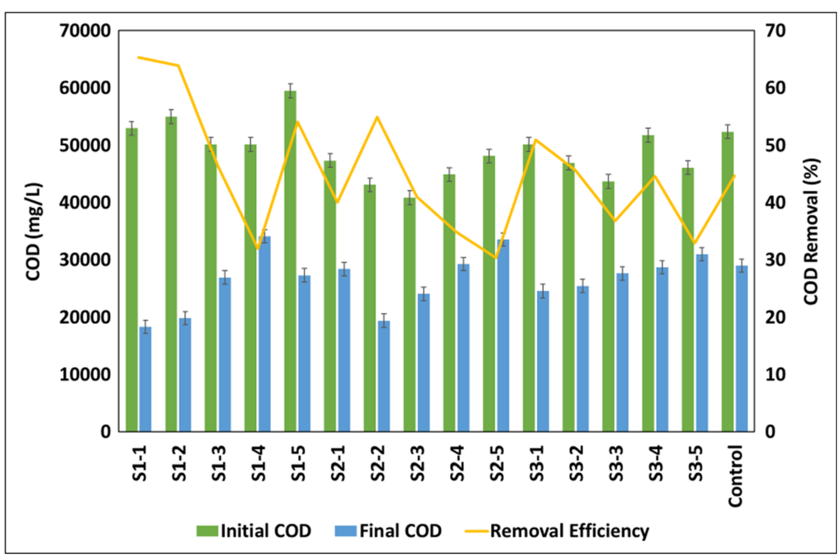

Fig. 5 Variations of COD concentrations and removal efficiencies

References

1. Tabak A, Kayabasi E, Guneser MT, Ozkaymak M (2019) Grey wolf optimization for optimum sizing and controlling of a PV/WT/BM hybrid energy system considering TNPC, LPSP, and LCOE concepts. Energy Sources, Part A 00:1–21. https://doi.org/10.1080/15567036.2019.1668880
2. Abdeshahian P, Lim JS, Ho WS, Hashim H, Lee CT (2016) Potential of biogas production from farm animal waste in Malaysia. Renew Sust Energ Rev 60:714–723. https://doi.org/10.1016/j.rser.2016.01.117
3. Tabak A, Ozkaymak M, Guneser MT, Erkol HO (2017) Optimization and evaluation of hybrid PV/WT/BM system in different initial costs and LPSP conditions. Int J Adv Comput Sci Appl 8:123–131. https://doi.org/10.14569/ijacsa.2017.081116
4. Abdallah MS, Hassaneen FY, Faisal Y, Mansour MS, Ibrahim AM, Abo-Elfadl S, Salem HG, Allam NK (2019) Effect of Ni-ferrite and Ni-Co-ferrite nanostructures on biogas production from anaerobic digestion. Fuel 254:115673. https://doi.org/10.1016/j.fuel.2019.115673
5. Hublin A, Zokić TI, Zelić B (2012) Optimization of biogas production from co-digestion of whey and cow manure. Biotechnol Bioprocess Eng 17:1284–1293. https://doi.org/10.1007/s12257-012-0044-z
6. Abdelsalam E, Samer M, Hassan HE, Badr Y (2015) Effect of $CoCl_2$, $NiCl_2$ and $FeCl_3$ additives on biogas and methane production. Misr J Eng 32:843–862. https://doi.org/10.21608/mjae.2015.98656
7. Kainthola J, Kalamdhad AS, Goud VV (2019) A review on enhanced biogas production from anaerobic digestion of lignocellulosic biomass by different enhancement techniques. Process Biochem 84:81–90. https://doi.org/10.1016/j.procbio.2019.05.023
8. Tabatabaei M, Aghbashlo M, Valijanian E, Kazemi Shariat Panahi H, Nizami AS, Ghanavati H, Sulaiman A, Mirmohamadsadeghi S, Karimi K (2020) A comprehensive review on recent biological innovations to improve biogas production, part 1: upstream strategies. Renew Energy 146:1204–1220. https://doi.org/10.1016/j.renene.2019.07.037
9. Brémond U, de Buyer R, Steyer JP, Bernet N, Carrere H (2018) Biological pretreatments of biomass for improving biogas production: an overview from lab scale to full-scale. Renew Sust Energ Rev 90:583–604. https://doi.org/10.1016/j.rser.2018.03.103
10. Romero-Güiza MS, Vila J, Mata-Alvarez J, Chimenos JM, Astals S (2016) The role of additives on anaerobic digestion: a review. Renew Sust Energ Rev 58:1486–1499. https://doi.org/10.1016/j.rser.2015.12.094
11. Nges IA, Björnsson L (2012) High methane yields and stable operation during anaerobic digestion of nutrient-supplemented energy crop mixtures. Biomass Bioenergy 47:62–70. https://doi.org/10.1016/j.biombioe.2012.10.002
12. Zhang L, Lee YW, Jahng D (2011) Anaerobic co-digestion of food waste and piggery wastewater: focusing on the role of trace elements. Bioresour Technol 102:5048–5059. https://doi.org/10.1016/j.biortech.2011.01.082
13. Mancini G, Papirio S, Riccardelli G, Lens PNL, Esposito G (2018) Trace elements dosing and alkaline pretreatment in the anaerobic digestion of rice straw. Bioresour Technol 247:897–903. https://doi.org/10.1016/j.biortech.2017.10.001
14. Zhang W, Zhang L, Li A (2015) Enhanced anaerobic digestion of food waste by trace metal elements supplementation and reduced metals dosage by green chelating agent [S, S]-EDDS via improving metals bioavailability. Water Res 84:266–277. https://doi.org/10.1016/j.watres.2015.07.010
15. Facchin V, Cavinato C, Fatone F, Pavan P, Cecchi F, Bolzonella D (2013) Effect of trace element supplementation on the mesophilic anaerobic digestion of foodwaste in batch trials: the influence of inoculum origin. Biochem Eng J 70:71–77. https://doi.org/10.1016/j.bej.2012.10.004
16. Janke L, Weinrich S, Leite AF, Schüch A, Nikolausz M, Nelles M, Stinner W (2017) Optimization of semi-continuous anaerobic digestion of sugarcane straw co-digested with filter cake: effects of macronutrients supplementation on conversion kinetics. Bioresour Technol 245:35–43. https://doi.org/10.1016/j.biortech.2017.08.084
17. Xu H, Yun S, Wang C, Wang Z, Han F, Jia B, Chen J, Li B (2020) Improving performance and phosphorus content of anaerobic co-digestion of dairy manure with aloe peel waste using vermiculite. Bioresour Technol 301:122753. https://doi.org/10.1016/j.biortech.2020.122753
18. Ye M, Liu J, Ma C, Li YY, Zou L, Qian G, Xu ZP (2018) Improving the stability and efficiency of anaerobic digestion of food waste using additives: a critical review. J Clean Prod 192:316–326. https://doi.org/10.1016/j.jclepro.2018.04.244
19. Weide T, Baquero CD, Schomaker M, Brügging E, Wetter C (2020) Effects of enzyme addition on biogas and methane yields in the batch anaerobic digestion of agricultural waste (silage, straw, and animal manure). Biomass Bioenergy 132:105442. https://doi.org/10.1016/j.biombioe.2019.105442
20. Yun S, Xing T, Han F, Shi J, Wang Z, Fan Q, Xu H (2021) Enhanced direct interspecies electron transfer with transition metal oxide accelerants in anaerobic digestion. Bioresour Technol 320:124294. https://doi.org/10.1016/j.biortech.2020.124294
21. Zhang T, Yun S, Li X, Huang X, Hou Y, Liu Y, Li J, Zhou X, Fang W (2017) Fabrication of niobium-based oxides/oxynitrides/nitrides and their applications in dye-sensitized solar cells and anaerobic digestion. J Power Sources 340:325–336. https://doi.org/10.1016/j.jpowsour.2016.11.082
22. Chen J, Yun S, Shi J, Wang Z, Abbas Y, Wang K, Han F, Jia B, Xu H, Xing T, Li B (2020) Role of biomass-derived carbon-based composite accelerants in enhanced anaerobic digestion: focusing on biogas yield, fertilizer utilization, and density functional theory calculations. Bioresour Technol 307:123204. https://doi.org/10.1016/j.biortech.2020.123204
23. Reuter M, Xiao Y, Boin U (2004) Recycling and environmental issues of metallurgical slags and salt fluxes. VII Int Conf Molten Slags Fluxes Salts 349–356
24. Jiang Y, Ling TC, Shi C, Pan SY (2018) Characteristics of steel slags and their use in cement and concrete—a review. Resour Conserv Recycl 136:187–197. https://doi.org/10.1016/j.resconrec.2018.04.023
25. Yi H, Xu G, Cheng H, Wang J, Wan Y, Chen H (2012) An overview of utilization of steel slag. Procedia Environ Sci 16:791–801. https://doi.org/10.1016/j.proenv.2012.10.108
26. EN 12457-2 Characterisation of waste leaching compliance test for leaching of granular waste materials and sludges
27. APHA (2005) Standard methods for the examination of water and wastewater. Am Public Heal Assoc Washington, DC, USA
28. Lim JW, Chew LH, Choong TSY, Tezara C, Yazdi MH (2016) Overview of steel slag application and utilization. MATEC Web Conf 74:3–7. https://doi.org/10.1051/matecconf/20167400026
29. Bankole LK, Rezan SA, Sharif NM (2014) Assessment of hexavalent chromium release in Malaysian electric arc furnace steel slag for fertilizer usage. IOP Conf Ser Earth Environ Sci 19:012004. https://doi.org/10.1088/1755-1315/19/1/012004
30. Guo J, Bao Y, Wang M (2018) Steel slag in China: treatment, recycling, and management. Waste Manag 78:318–330. https://doi.org/10.1016/j.wasman.2018.04.045
31. Michael T. Madigan, John M. Martinko, Kelly S. Bender, Daniel H. Buckley DAS (2015) Brock biology of microorganisms, 14th ed, Pearson, USA
32. Liu L, Zhang T, Wan H, Chen Y, Wang X, Yang G, Ren G (2015) Anaerobic co-digestion of animal manure and wheat straw for

optimized biogas production by the addition of magnetite and zeolite. Energy Convers Manag 97:132–139. https://doi.org/10.1016/j.enconman.2015.03.049
33. Shen R, Jing Y, Feng J, Luo J, Yu J, Zhao L (2020) Performance of enhanced anaerobic digestion with different pyrolysis biochars and microbial communities. Bioresour Technol 296:122354. https://doi.org/10.1016/j.biortech.2019.122354
34. Baniamerian H, Isfahani PG, Tsapekos P, Alvarado-Morales M, Shahrokhi M, Vossoughi M, Angelidaki I (2019) Application of nano-structured materials in anaerobic digestion: current status and perspectives. Chemosphere 229:188–199. https://doi.org/10.1016/j.chemosphere.2019.04.193
35. Han F, Yun S, Zhang C, Xu H, Wang Z (2019) Steel slag as accelerant in anaerobic digestion for nonhazardous treatment and digestate fertilizer utilization. Bioresour Technol 282:331–338. https://doi.org/10.1016/j.biortech.2019.03.029
36. Ma W, Xin H, Zhong D, Qian F, Han H, Yuan Y (2015) Effects of different states of Fe on anaerobic digestion: a review. J Harbin Instiyue Technol 22:69–75. https://doi.org/10.11916/j.issn.1005-9113.2015.06.010
37. Matheri AN, Ntuli F, Ngila JC (2021) Sludge to energy recovery dosed with selected trace metals additives in anaerobic digestion processes. Biomass Bioenergy 144:105869. https://doi.org/10.1016/j.biombioe.2020.105869
38. Xu H, Chang J, Wang H, Liu Y, Zhang X, Liang P, Huang X (2019) Enhancing direct interspecies electron transfer in syntrophic-methanogenic associations with (semi) conductive iron oxides: effects and mechanisms. Sci Total Environ 695:133876. https://doi.org/10.1016/j.scitotenv.2019.133876
39. Yun S, Zhang C, Wang Y, Zhu J, Huang X, du T, Li X, Wei Y (2019) Synergistic effects of Fe salts and composite additives on anaerobic digestion of dairy manure. Int Biodeterior Biodegrad 136:82–90. https://doi.org/10.1016/j.ibiod.2018.10.011
40. Salama ES, Jeon BH, Kurade MB, Patil SM, Usman M, Li X, Lim H (2020) Enhanced anaerobic co-digestion of fat, oil, and grease by calcium addition: boost of biomethane production and microbial community shift. Bioresour Technol 296:122353. https://doi.org/10.1016/j.biortech.2019.122353
41. Wang Y, Ren G, Zhang T, Zou S, Mao C, Wang X (2017) Effect of magnetite powder on anaerobic co-digestion of pig manure and wheat straw. Waste Manag 66:46–52. https://doi.org/10.1016/j.wasman.2017.04.031
42. Peng H, Zhang Y, Tan D, Zhao Z, Zhao H, Quan X (2018) Roles of magnetite and granular activated carbon in improvement of anaerobic sludge digestion. Bioresour Technol 249:666–672. https://doi.org/10.1016/j.biortech.2017.10.047
43. Xie S, Li X, Wang C, Kulandaivelu J, Jiang G (2020) Enhanced anaerobic digestion of primary sludge with additives: performance and mechanisms. Bioresour Technol 316:123970. https://doi.org/10.1016/j.biortech.2020.123970
44. Zheng M, Li X, Li L, Yang X, He Y (2009) Enhancing anaerobic biogasification of corn stover through wet state NaOH pretreatment. Bioresour Technol 100:5140–5145. https://doi.org/10.1016/j.biortech.2009.05.045
45. Zhang C, Yun S, Li X, Wang Z, Xu H, du T (2018) Low-cost composited accelerants for anaerobic digestion of dairy manure: focusing on methane yield, digestate utilization and energy evaluation. Bioresour Technol 263:517–524. https://doi.org/10.1016/j.biortech.2018.05.042