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ORIGINAL ARTICLE

Investigation of the effects of blast furnace slag ratio, total solid, and pH on anaerobic digestion: modeling and optimization by using response surface methodology

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Abstract

In this study, it is aimed to optimize the anaerobic digestion (AD) system in which blast furnace slag (BFS) is used as an additive by using the response surface methodology (RSM). For this purpose, BFS ratio (0.5–3%), pH (5–9), and initial total solid (TS) (6–10%) were selected as input parameters and a model was successfully developed in RSM with Box-Behnken (BB) design for optimization of cumulative biogas production (mL), biogas yield (mL/g VS), CH_4 content (%), volatile solids (VS) reduction (%), and chemical oxygen demand (COD) removal (%). Coefficient values (R^2) obtained from analysis of variance (ANOVA) were highly significant for cumulative biogas production, biogas yield, CH_4 content, VS reduction, and COD removal as 0.94, 0.95, 0.96, 0.94, and 0.94, respectively. RSM results showed that optimum conditions for the maximum output values were obtained as 2.01%, 9 and 10% for BFS ratio, pH, and TS, respectively. Corresponding to these conditions, the maximum biogas production, biogas yield, CH_4, VS reduction, and COD removal were 15,420 mL, 543.23 mL/g VS, 76.30%, 61.12%, and 70.85%, respectively.

Keywords Anaerobic digestion · Additive · Optimization · Response surface methodology

1 Introduction

Increasing demand for energy, which has an important role in the economic prosperity of countries, causes energy crises to occur today. For meeting the energy needs, fossil fuels which will be depleted in the near future and negatively affect human and nature by causing air pollution and global warming as a result of the release of greenhouse gases such as carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) are used. These negative effects have recently led scientists to research to develop new sources that will be alternative to fossil fuels. Thus, interest in AD, which uses different biomass resources, has also started to increase [1–4]. Biogas, which is produced as a result of AD of industrial, agricultural, and animal wastes by microorganisms in an oxygen-free environment, is a clean and renewable energy source containing mainly 55–75% CH_4 and 25–45% CO_2 by volume [5–8]. AD is a complex process in which various types of microorganisms take part in each stage of hydrolysis, acidogenesis, acetogenesis, and methanogenesis, respectively, in the degradation of organic matter [9]. Hydrolysis, which is the first one of these stages in AD, is known as the rate limiting step because lignocellulose, hemicellulose, and lignin, which are found in organic substances and are very difficult to digest, create high ammonium inhibition in the environment and reduce the hydrolysis rate and methane yield [10–12]. Nowadays, AD technology which produces biogas is developing rapidly, but factors such as poor process stability, long hydraulic retention time, slow growth rates of anaerobic microorganisms, low buffering capacity, and low biogas yield due to low biodegradation efficiency limit the availability of biogas [13–15]. In addition, in order to maintain the stability of AD reactors and prevent the accumulation of volatile fatty acids (VFA), the factors affecting AD performance such as substrate, temperature, and pH should be controlled carefully [16, 17]. In order to reduce all these obstacles and increase the biogas yield, different strategies such as optimization of the amount of solid matter in order

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to obtain better mass transfer, adding buffering substances to the reactor to ensure the optimum pH for the bacteria, and physical, chemical, and biological pre-treatments are applied [10, 18]. On the other hand, another way to achieve more biogas production by improving AD performance is to add additives to the reactors that provide more organic matter breakdown by providing suitable digestion conditions for microorganisms [19, 20]. Studies conducted so far researchers have added to reactors biological additives including fungal, bacterial, and enzymes [11, 21], trace elements [2], biochar [22], activated carbon [23], magnetite and zeolite [24], metal oxides [25], and slags [26] and examined their effects on biogas production and methane yield. BFS is an inevitable by product of pig iron production that occurs huge amount and contains strong alkaline structure and significant metal ions. BFS, which is occurred between 250 and 420 kg per ton of hot iron produced as a result of pyrometallurgical processes, is a major waste source if not recycled and used in appropriate ways [27]. BFS contains 0.5–0.8% FeO, 35–42% CaO, 35–40% SiO_2, 8–9% MgO, 8–15% Al_2O_3, 0.3–0.1% MnO, and 0.7–1.5% S by weight [28]. Thanks to the microelements in its content, it has the potential to be used as an additive in the AD system [26].

However, since obtaining maximum efficiency by determining the optimum values of these parameters that affect biogas production brings with it too much cost and extra time due to the excess number of tests, statistical programs are started to be used instead of traditional methods [29]. Today, in order to reduce the number of tests, RSM is a widely used technique in which output factors are optimized with test variables with the development of computer programs [30].

Deepanraj et al. [31] applied RSM for estimation and optimization of total biogas production and COD removal using parameters of solid concentration (5–15%), pH (5–9), temperature (30–60 °C), and co-digestion (0–40%). When the results are examined, the optimum values corresponding to solids concentration 7.38%, pH value 7, temperature 48.43 °C, and co-digestion 29% were obtained from RSM as 6344 mL total amount of biogas and 39% COD removal. Also, the overall desirability value was obtained as 0.94. Safari et al. [32] used the RSM and BB design to determine the effects of inoculum, TS, temperature, and stirring time in AD where they use cattle manure and canola residues and optimize the biogas yield. It was observed in experimental results that temperature change had a great effect on methane yield and optimum values were obtained as 52.49 °C of temperature, 3.12 min day^{-1} of stirring time, 7.02% TS of substrate working volume, and 22.17% inoculum in thermophilic conditions. Methane yield at these values was 403.63 L/kgVS. In mesophilic conditions, 376.76 L/kgVS methane yield was observed at 3.57 min day^{-1} of stirring time, 7.41% TS of substrate working volume, 26.26% inoculum, and temperature at 40.36 °C. The highest R^2 value (0.9983) showed that the model can be used in methane production estimation. Menon et al. [33] designed an RSM model to examine the effect of adding trace metals (Ca, Mg, Co, and Ni) to the reactor as micronutrient supplements on biogas yield. Optimum concentrations for optimum biogas production and methane yield were obtained as 303, 777, 7, and 3 mg/L Ca, Mg, Co, and Ni in the RSM model, respectively. Yılmaz et al. [29] performed a model and optimization process in RSM for the estimation of cumulative biogas production, methane content (CH_4%), and COD removal (%) in anaerobic digestion. For this, total solid percentage (TS%), inoculum ratio (%), the amount of pumice (g L^{-1}), and particle size of pumice (mm) were selected as input parameters. As a result of ANOVA analysis, R^2 values were obtained as 0.98, 0.98, and 0.99 for cumulative biogas production, CH_4 (%), and COD removal (%), respectively, which showed that it was acceptable for the relationship between the input parameters and responses.

While there are studies investigating the effect of different additives on biogas and methane yield in the literature, no studies related to the optimization of BFS addition have been found. It was thought that this gap should be filled by conducting this study and for this purpose, a model was created in RSM for the estimation and optimization of cumulative biogas production (mL), biogas yield (mL/gVS), CH_4 content (%), VS reduction (%), and COD removal (%). This study aims to reduce the number of tests and TS (%), pH, and BFS ratio (%) were selected as input parameters.

2 Materials and methods

2.1 Characterization of cattle manure and inoculum

Cattle manure used as substrate was collected from a local animal breeding farm located in Karabük, Turkey. The inoculum was taken from the 40 L biogas system with a mixture of cattle and poultry manure in the Environmental Engineering Laboratory. The results of the analyzes made to determine the characteristics of the cattle manure and inoculum are given in Table 1. The BFS to be used as an additive was obtained from the integrated iron-steel production plant and dried in an oven at 105 °C for 24 h before being used in the biogas system. Since the particle size is smaller than 0.5 mm, the grinding process has not been done.

2.2 Analytical methods

The amount of biogas produced was measured daily according to the water displacement principle. The biogas composition (CH_4, CO_2, H_2S, and O_2) in the produced biogas was measured with a biogas analyzer (GEOTECH 5000, UK).

Table 1 Characteristics of cattle manure and inoculum

	Cattle manure	Inoculum
C (%)	45.59	35.17
N (%)	7.18	3.91
C/N	6.35	8.99
TS (%)	27.18	14.58
VS (%)	91.57	92.60
VFA (mg/L)	61,200	-
Total nitrogen (mg/L)	14,521	-
Chemical oxygen demand, COD (mg/L)	49,284	31,346

The elemental analyzer (Flash 2000 Element Analyzer) was used for measuring carbon (C) and nitrogen (N). The parameters of COD, TS, and VS analysis were performed according to the Standart Methods of the American Public Health Association [34]. The pH values of the reactors at the first day and at the end of the experiment were measured with a WTW720i pH meter.

2.3 Experimental setup

A fed-batch biogas system was established to carry out the experiments. The schematic view of the experimental setup is shown in Fig. 1. In the system using 1-L glass reactors, experiments were carried out in 600-mL working volume with 100 mL of inoculum and blast furnace slag added at concentrations of 0.5, 1, 1.5, 2, 2.5, and 3 wt%. Liquid gasket is used to prevent gas leakage that may occur in the reactors, and glass bottles are painted black to protect microorganisms from light. The tightness of the reactors, which were connected by using pneumatic equipment, was checked by a hand pump. The experiments were run in mesophilic conditions (36 ± 1 °C) for 30 days in duplicate. 1 N hydrochloric acid (HCl) and 1 N sodium hydroxide (NaOH) were used to achieve the desired pH values. Finally, N_2 gas was passed through all the reactors for 5 min to obtain environment required for anaerobic digestion by removing oxygen.

2.4 Statistical model

RSM is a mathematical technique that can determine the best experimental conditions by considering the relationship between more than one independent variable and the dependent variable. As one of the RSM models, the BB design can be optimized according to the input data and so it saves both time and money with less experimentation [35]. BB design was chosen to optimization of biogas production under different conditions and working principle of the model is illustrated in Fig. 2. While cumulative biogas production (mL), biogas yield (mL/gVS), CH_4 content (%), VS reduction (%), and COD removal (%) were chosen as response variables, pH, TS (%), and BFS ratio (%) were used as input parameters. Table 2 shows the input variables and levels. By using these input parameters, optimization and estimation of the test results were carried out in Minitab 17 software with 15 experiment sets and the data are given in Table 3. In RSM, each input parameter for biogas system is assumed to be computable and can be expressed as [36]:

$$y = f(x_1, x_2, \dots, x_n) \tag{1}$$

where x_1, x_2, ⋯, x_n are input parameters and y is output, respectively. In the first stage of RSM where there is an appropriate relationship between output and input parameters, a quadratic equation is applied for this correlation and given in Eq. (2) [37]:

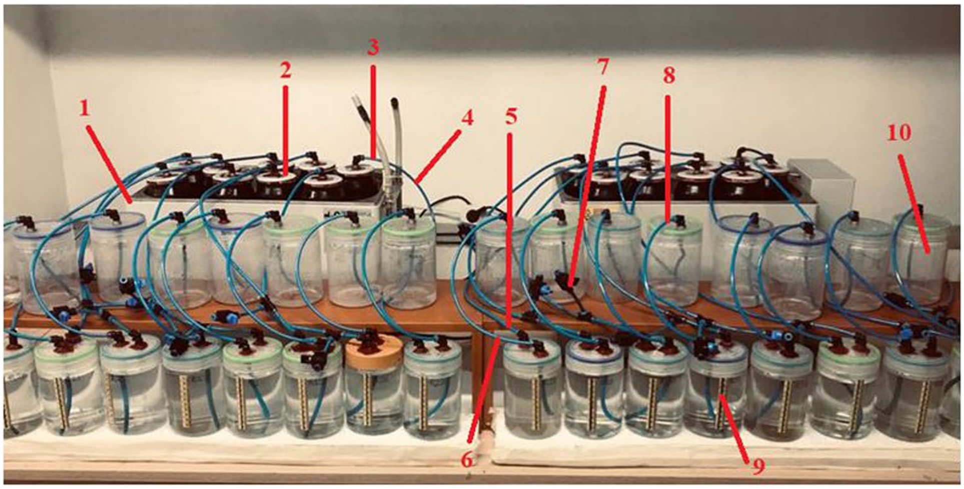
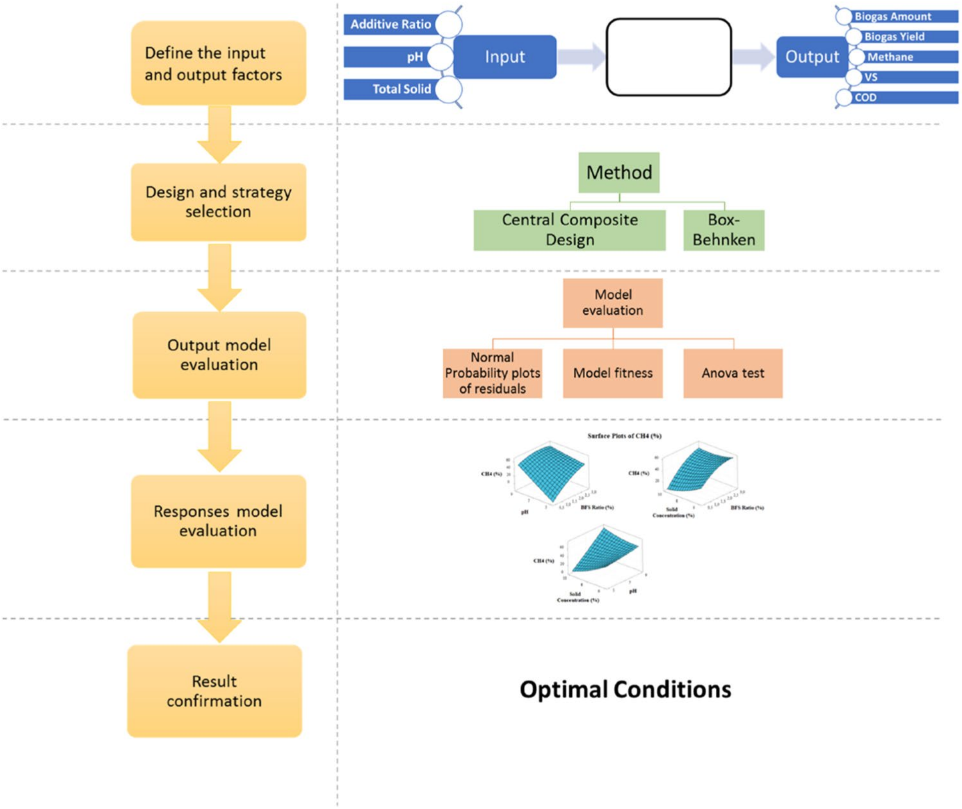


Fig. 1 Experimental setup: 1, temperature controlled water bath; 2, digester; 3, biogas outlet; 4, biogas tube; 5, biogas inlet; 6, water outlet; 7, biogas sampling point; 8, water inlet; 9, biogas collecting bottle; 10, water collecting bottle

Fig. 2 Flowchart of the model



$$y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\sum_{j\geq i}^{k}\beta_{ij}x_i x_j + \sum_{i=1}^{k}\beta_{ii}x_i^2 + \varepsilon \quad (2)$$

where i is the linear coefficient, j is the second-order coefficient, β is the regression coefficient, k is the number of parameters, and ε is the error discovered in the response. ANOVA including p-value and f-value was used to calculate the regression model.

3 Results and discussion

3.1 Daily and cumulative biogas/methane production from experiments

Cumulative and daily biogas productions of all groups are given in Fig. 3a and 3b. The highest biogas production was observed in R5 where TS is 10%, pH 9, and BFS ratio 1% with 12,870.6 mL. It has been determined that increasing BFS ratios at pH 9 have a negative effect on biogas production. As seen in Table 3, the highest biogas production in all reactors was measured as 11,551.1, 8959.3, 10,270.9, and 9776.1 mL for R2, R8, R10, and R15, respectively, according to pH 9 and rising BFS ratio. In addition, the highest biogas yields were also reached at pH 9 in R5, R8, and R2 with 472.3, 412.1, and 406.0 mL/g VS, respectively. After the reactors with pH 9, the highest biogas productions were obtained in the reactors with pH 7 at R9, R11, and R14 with 8762.9, 6909.4, and 5770.6 mL, respectively. The experiments conducted at pH 5 showed the lowest biogas productions and biogas yields. In the AD system, pH is one of the most important key parameters and directly affects the performance of the microorganism groups in the reactor [38]. As can be seen from Table 3, in all reactors with an initial pH 9, after 30 days of hydraulic retention time (HRT), the intra-reactor pH values vary between 7.36 and 7.22. In the light of these

Table 2 Input factors and levels for optimization

Input factors	Code	Levels					
Blast furnace slag ratio (%w)	A	0.5	1.0	1.5	2.0	2.5	3.0
TS (%)	B	6	8	10			
pH	C	5	7	9			

Table 3 Box-Behnken design and the experimental results

Reactor	Std order	Run order	BFS ratio (w%)	TS (%)	pH (initial)	pH (final)	Cumulative produced biogas (mL)	Biogas yield (mL/gVS)	CH_4 content (%)	VS reduction (%)	COD removal (%)
R1	15	1	0.5	6	5	5.27 ± 0.02	288.5 ± 42.2	13.1 ± 36.2	15.6 ± 2.7	7.67 ± 0.8	9.52 ± 1.1
R2	9	2	0.5	10	9	7.23 ± 0.01	11,551.1 ± 325.4	406.0 ± 82.4	61.5 ± 5.9	51.13 ± 2.9	54.26 ± 6.8
R3	4	3	1	6	5	5.63 ± 0.03	783.3 ± 53.7	37.3 ± 53.7	28.0 ± 3.4	11.66 ± 1.1	15.08 ± 2.4
R4	5	4	1	8	7	5.71 ± 0.01	1066 ± 124.1	44.8 ± 75.4	26.6 ± 3.9	19.80 ± 2.3	11.95 ± 1.7
R5	7	5	1	10	9	7.36 ± 0.02	12,870.6 ± 324.9	472.3 ± 82.6	62.5 ± 4.8	52.64 ± 4.3	62.45 ± 7.3
R6	6	6	1.5	8	5	5.35 ± 0.04	351.3 ± 51.6	14.6 ± 28.8	22.5 ± 1.6	6.24 ± 0.5	15.54 ± 2.4
R7	12	7	1.5	10	7	5.75 ± 0.05	1262.4 ± 135.5	44.7 ± 65.7	30.0 ± 2.2	11.69 ± 1.4	14.89 ± 1.7
R8	1	8	1.5	6	9	7.25 ± 0.03	8959.3 ± 259.1	412.1 ± 52.3	61.9 ± 4.6	47.32 ± 3.6	42.17 ± 5.3
R9	13	9	2	6	7	7.14 ± 0.01	6909.4 ± 183.7	267.2 ± 45.4	60.1 ± 3.9	49.45 ± 3.3	52.1 ± 6.3
R10	3	10	2	8	9	7.35 ± 0.06	10,270.9 ± 322.6	401.8 ± 77.1	62.0 ± 4.6	52.01 ± 5.3	59.77 ± 6.9
R11	2	11	2.5	10	7	6.83 ± 0.02	8762.9 ± 216.7	305.8 ± 65.2	55.8 ± 4.8	40.82 ± 4.1	31.68 ± 5.4
R12	8	12	2.5	6	9	7.22 ± 0.01	7710.5 ± 143.2	405.2 ± 31.3	58.9 ± 5.0	35.90 ± 3.5	27.27 ± 3.2
R13	10	13	3	10	5	5.79 ± 0.03	673.3 ± 52.8	23.4 ± 40.5	31.4 ± 1.7	16.27 ± 2.6	14.36 ± 2.0
R14	11	14	3	6	7	7.1 ± 0.05	5770.6 ± 96.4	311.4 ± 30.8	57.1 ± 2.3	30.99 ± 2.7	45.39 ± 4.6
R15	14	15	3	8	9	7.34 ± 0.04	9776.1 ± 118.8	400.2 ± 48.7	61.9 ± 3.8	35.16 ± 3.3	47.88 ± 3.9

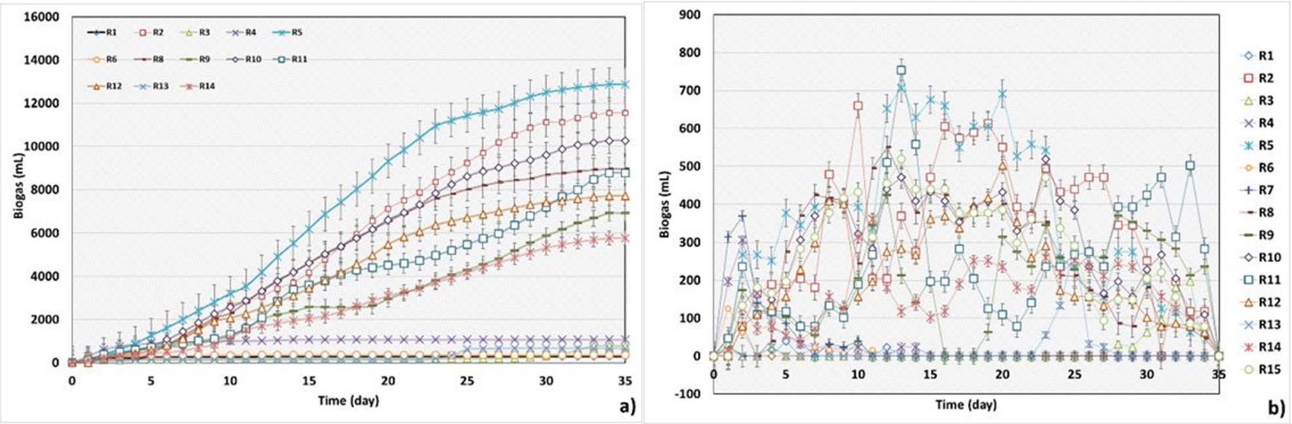


Fig. 3 Cumulative (**a**) and daily (**b**) biogas productions

results, and very recently, in our group's study on the use of BFS as an additive in the anaerobic system, it was seen that BFS improved the buffering capacity when compared to the results of the control group in which BFS was not added [26]. Kim et al. [39] explained that adding BFS to fermentation reactor could result with a decrease of pH due to short-chain carboxylates (SCCs) production. Our experimental results also support this phenomenon.

From Table 3, it is seen that the addition of BFS at high pH value has a positive effect on CH_4 production. The highest methane content was reached with 62.5%, 62%, and 61.9% in R5, R10, and R15 where pH 9, respectively. Kim et al. [39] mentioned that adding BFS to AD inhibited the methanogenesis due to high alkali conditions but our results showed that adding BFS to the AD system at pH 9 and in all BFS ratios improved the CH_4 content of the produced biogas compared to the other reactor.

3.2 Simultaneous effect of BFS ratio, solid concentration, and pH

ANOVA is one of the most important tools to attain the best suitable mathematical model to define the importance and property of quadratic mathematical regression model [40]. ANOVA results are given in Table 4 and Table 5. *p*-value is the most important parameter in ANOVA results that must be maximum 0.05. If the *p*-value is higher than 0.05, it is thought to be the model is insignificant and if the *p*-value is lower than 0.05, it is thought to be the effect of this factor on the developed model is greater [41]. As seen in Table 4,

Table 4 ANOVA results of cumulative biogas, biogas yield, and CH_4

Source	Cumulative biogas (mL)			Biogas yield (mL/gVS)			CH_4 (%)		
	Contribution	*F*-value	*p*-value	Contribution	*F*-value	*p*-value	Contribution	*F*-value	*p*-value
Model	94.14%	8.92	0.013	95.37%	11.45	0.008	96.45%	15.09	0.004
Linear	78.81%	16.23	0.005	84.85%	18.04	0.004	80.97%	25.64	0.002
A — BFS ratio (%)	1.51%	8.02	0.037	4.95%	9.45	0.028	13.05%	24.75	0.004
B — pH	76.51%	39.25	0.002	79.32%	45.23	0.001	67.59%	55.15	0.001
C — TS (%)	0.80%	1.03	0.357	0.59%	3.01	0.143	0.34%	7.81	0.038
Square	3.07%	0.58	0.651	3.87%	0.81	0.539	4.16%	1.27	0.379
A^2	0.57%	1.32	0.303	0.64%	0.92	0.382	0.01%	3.19	0.134
B^2	0.39%	0.83	0.404	0.51%	1.55	0.268	0.10%	0.12	0.747
C^2	2.10%	0.37	0.571	2.72%	1.04	0.354	4.05%	0.95	0.375
2-way interaction	12.26%	3.48	0.106	6.65%	2.40	0.184	11.32%	5.31	0.052
A*B	0.11%	3.45	0.122	0.19%	2.43	0.180	1.83%	9.34	0.028
A*C	0.00%	1.66	0.254	0.13%	0.44	0.538	0.03%	1.47	0.280
B*C	12.14%	10.36	0.024	6.33%	6.84	0.047	9.46%	13.32	0.015
Error	5.86%			4.63%			3.55%		
Total	100.00%			100.00%			100.00%		

Table 5 ANOVA results of VS reduction and COD removal

Source	VS reduction (%)			COD removal (%)		
	Contribution	*F*-value	*p*-value	Contribution	*F*-value	*p*-value
Model	93.59%	8.12	0.016	94.19%	9.01	0.013
Linear	68.98%	15.54	0.006	59.14%	15.21	0.006
A — BFS ratio (%)	1.35%	7.34	0.042	1.96%	18.95	0.007
B — pH	67.62%	40.95	0.001	57.18%	28.91	0.003
C — TS (%)	0.00%	7.69	0.039	0.00%	9.34	0.028
Square	3.93%	1.17	0.409	0.59%	1.79	0.265
A^2	0.20%	2.51	0.174	0.21%	3.81	0.109
B^2	0.26%	0.17	0.701	0.00%	0.59	0.477
C^2	3.47%	0.00	0.986	0.38%	0.79	0.415
2-way interaction	20.68%	5.38	0.050	34.46%	9.88	0.015
A*B	5.45%	13.18	0.015	4.54%	14.77	0.012
A*C	1.72%	5.37	0.068	0.84%	1.28	0.309
B*C	13.52%	10.55	0.023	29.08%	25.02	0.004
Error	6.41%			5.81%		
Total	100.00%			100.00%		

p-values of BFS ratio and pH are lower than 0.05 and greater than 0.05 for TS ratio for cumulative biogas production in terms of linear coefficients. *p*-values for second-order coefficients of all factors are greater than 0.05 and these results mean that pH has more effect on cumulative biogas production. For biogas yield, *p*-values of additive ratio and pH are lower than 0.05 while *p*-value of solid ratio is greater than 0.05. *p*-values for second-order coefficients of all factors are greater than 0.05 again and the most influential factor is pH for biogas yield. *p*-values of all factors are lower than 0.05 for CH_4 and the second-order coefficients are greater than 0.05 so it can be say all factor are important for CH_4 production. ANOVA results of VS reduction and COD removal are given in Table 5. *p*-values of all factors are higher than 0.05 for both VS reduction and COD removal and that means all factors are important for VS reduction and COD removal.

In order to show that the model was fit to give the most accurate results, R^2 values, which should be between 0.75 and 1, were calculated as given in Eq. (3) [41]. R^2 values for cumulative biogas, COD removal, VS reduction, CH_4, and biogas yield are 94.14%, 94.19%, 93.59%, 96.45%, and 95.37%, respectively. These results showed that the evaluated model was highly significant.

$$R^2 = 1 - \frac{SS_{\text{error}}}{SS_{\text{model}} + SS_{\text{error}}} \tag{3}$$

where SS_{model} represents the sum of the squares of the model, while SS_{error} represents the sum of the squares of the error. Predicted and observed data correlations are given for cumulative biogas production, biogas yield, CH_4, VS reduction, and COD removal in Fig. 4a, b, c, d, and e, respectively. As can be seen from Fig. 4a–e, the experimental data and predicted values for each response are in a good correlation. Also, the second-order equations created by RSM are given between Eqs. (4) and (8) depending on the input parameters.

$$\begin{aligned}\text{Cumulative biogas (mL)} = {} & 59886 + 8633\mathbf{BFSRatio}(\%) \\ & - 7438\mathbf{pH} - 11849\mathbf{TS}(\%) \\ & - 1096\mathbf{BFSRatio}(\%) * \mathbf{BFSRatio}(\%) \\ & + 275\mathbf{pH} * \mathbf{pH} + 193\mathbf{TS}(\%) * \mathbf{TS}(\%) \\ & - 1043\mathbf{BFSRatio}(\%) * \mathbf{pH} \\ & + 650\mathbf{BFSRatio}(\%) * \mathbf{TS}(\%) \\ & + 1025\mathbf{pH} * \mathbf{TS}(\%)\end{aligned} \tag{4}$$

$$\begin{aligned}\text{Biogas Yield}\left(\frac{\text{mL}}{\text{gVS}}\right) = {} & 2166 + 338\mathbf{BFSRatio}(\%) \\ & - 261\mathbf{pH} - 436\mathbf{TS}(\%) \\ & - 32.3\mathbf{BFSRatio}(\%) * \mathbf{BFSRatio}(\%) \\ & + 13.2\mathbf{pH} * \mathbf{pH} + 11.5\mathbf{TS}(\%) * \mathbf{TS}(\%) \\ & - 30.8\mathbf{BFSRatio}(\%) * \mathbf{pH} \\ & + 11.7\mathbf{BFSRatio}(\%) * \mathbf{TS}(\%) \\ & + 29.3\mathbf{pH} * \mathbf{TS}(\%)\end{aligned} \tag{5}$$

$$\begin{aligned}\text{CH4}(\%) = {} & 196.8 + 54.0\mathbf{BFSRatio}(\%) \\ & - 13.4\mathbf{pH} - 46.7\mathbf{TS}(\%) \\ & - 5.17\mathbf{BFSRatio}(\%) * \mathbf{BFSRatio}(\%) \\ & + 0.312\mathbf{pH} * \mathbf{pH} + 0.941\mathbf{TS}(\%) * \mathbf{TS}(\%) \\ & - 5.20\mathbf{BFSRatio}(\%) * \mathbf{pH} \\ & + 1.85\mathbf{BFSRatio}(\%) * \mathbf{TS}(\%) \\ & + 3.523\mathbf{pH} * \mathbf{TS}(\%)\end{aligned} \tag{6}$$

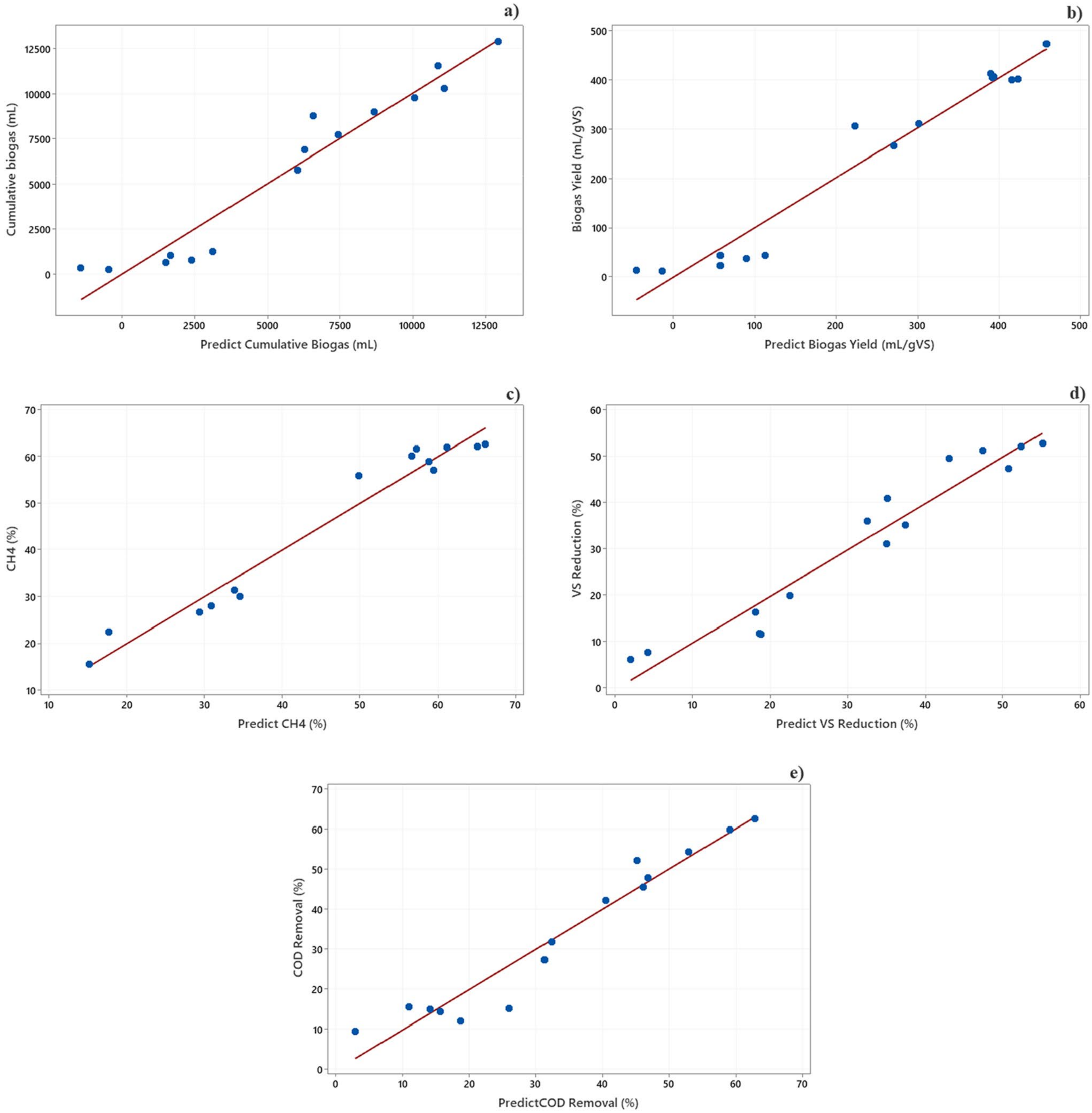


Fig. 4 Predicted and observed data correlations: **a** cumulative biogas, **b** biogas yield, **c** CH_4, **d** VS reduction, **e** COD removal

$$\begin{aligned}\text{VS Reduction }(\%) =\ & 128 + 50.9\mathbf{BFSRatio}(\%) \\ & - 0.6\mathbf{pH} - 41.5\mathbf{TS}(\%) \\ & - 6.02\mathbf{BFSRatio}(\%) * \mathbf{BFSRatio}(\%) \\ & - 0.49\mathbf{pH} * \mathbf{pH} - 0.02\mathbf{TS}(\%) * \mathbf{TS}(\%) \\ & - 8.11\mathbf{BFSRatio}(\%) * \mathbf{pH} \\ & + 4.65\mathbf{BFSRatio}(\%) * \mathbf{TS}(\%) \\ & + 4.12\mathbf{pH} * \mathbf{TS}(\%)\end{aligned} \tag{7}$$

$$\begin{aligned}\text{COD Removal }(\%) =\ & 224 + 88.2\mathbf{BFSRatio}(\%) \\ & - 40.9\mathbf{pH} - 37.3\mathbf{TS}(\%) \\ & - 7.75\mathbf{BFSRatio}(\%) * \mathbf{BFSRatio}(\%) \\ & + 0.96\mathbf{pH} * \mathbf{pH} - 1.18\mathbf{TS}(\%) * \mathbf{TS}(\%) \\ & - 8.97\mathbf{BFSRatio}(\%) * \mathbf{pH} \\ & + 2.38\mathbf{BFSRatio}(\%) * \mathbf{TS}(\%) \\ & + 6.63\mathbf{pH} * \mathbf{TS}(\%)\end{aligned} \tag{8}$$

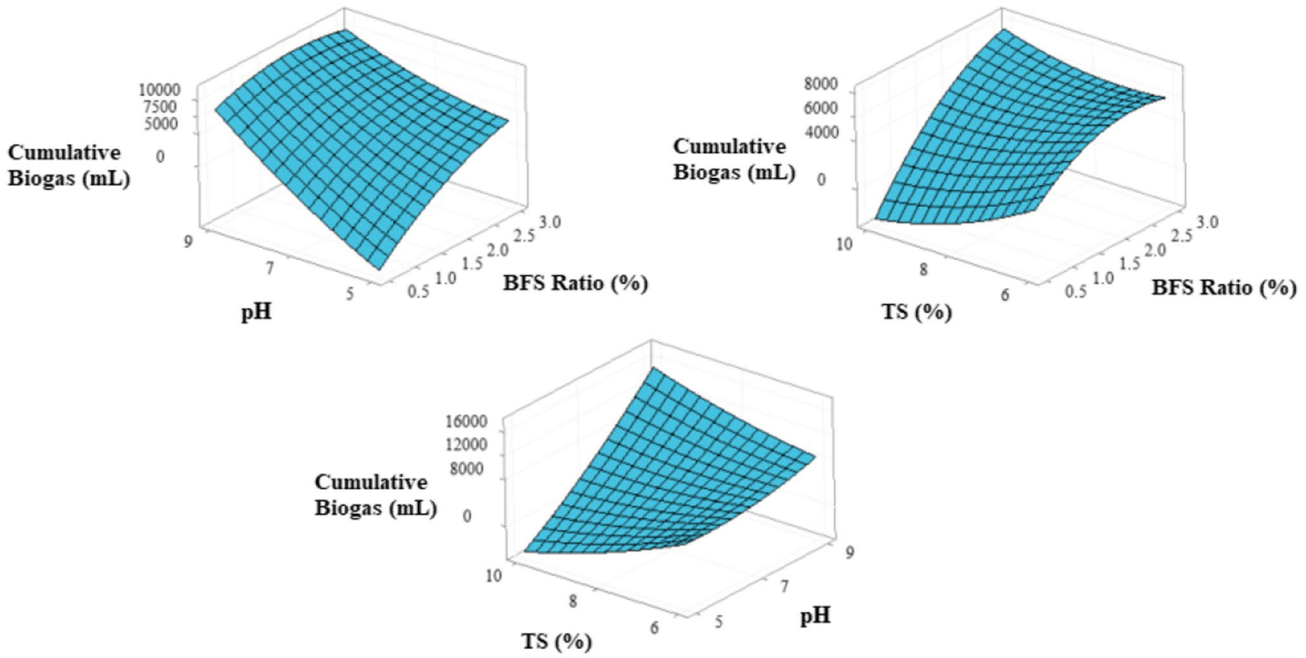


Fig. 5 Response surface plots of cumulative biogas

The synergetic effects of the selected responses are determined by three-dimensional response surface graphs and are shown in Figs. 5, 6, 7, 8, and 9. As seen from Fig. 5, the cumulative biogas production increased due to the increase in initial pH (from 5 to 9). pH adjustment in the range of 5.0–11.0 can lead to an increased solubilization of the organics which can turned a fraction of the recalcitrant material into a more degradable form [42]. It is

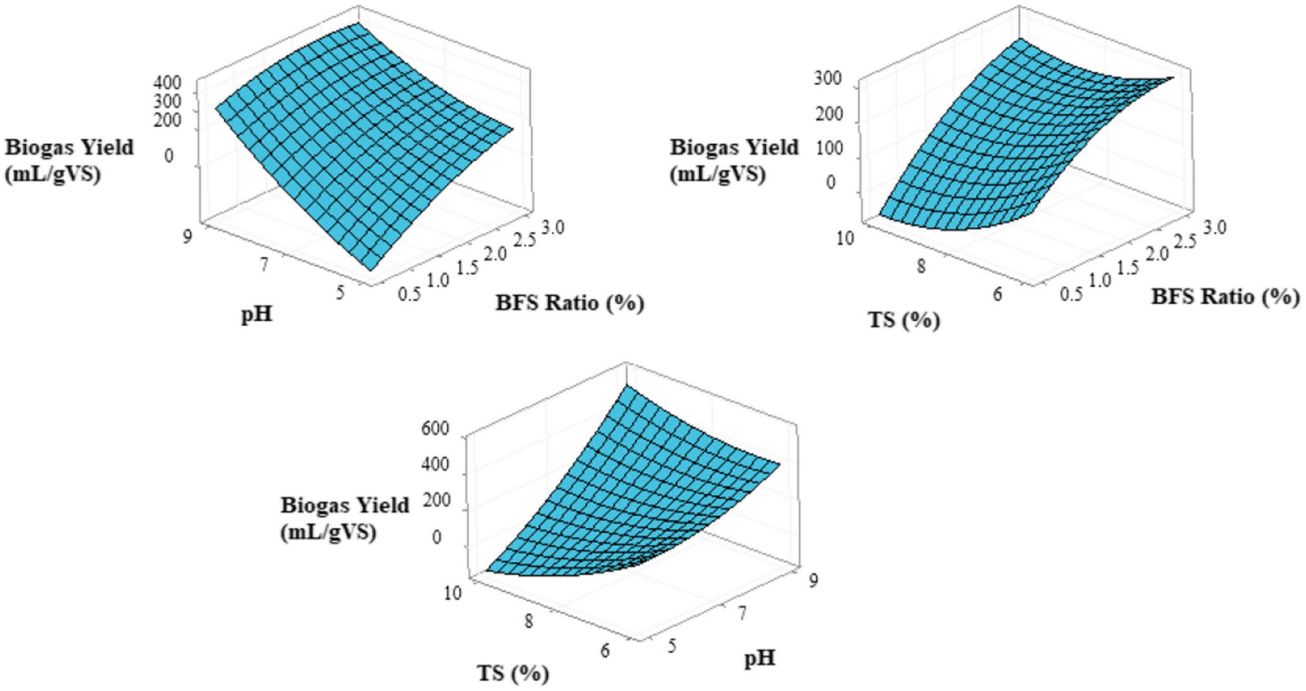


Fig. 6 Response surface plots of biogas yield

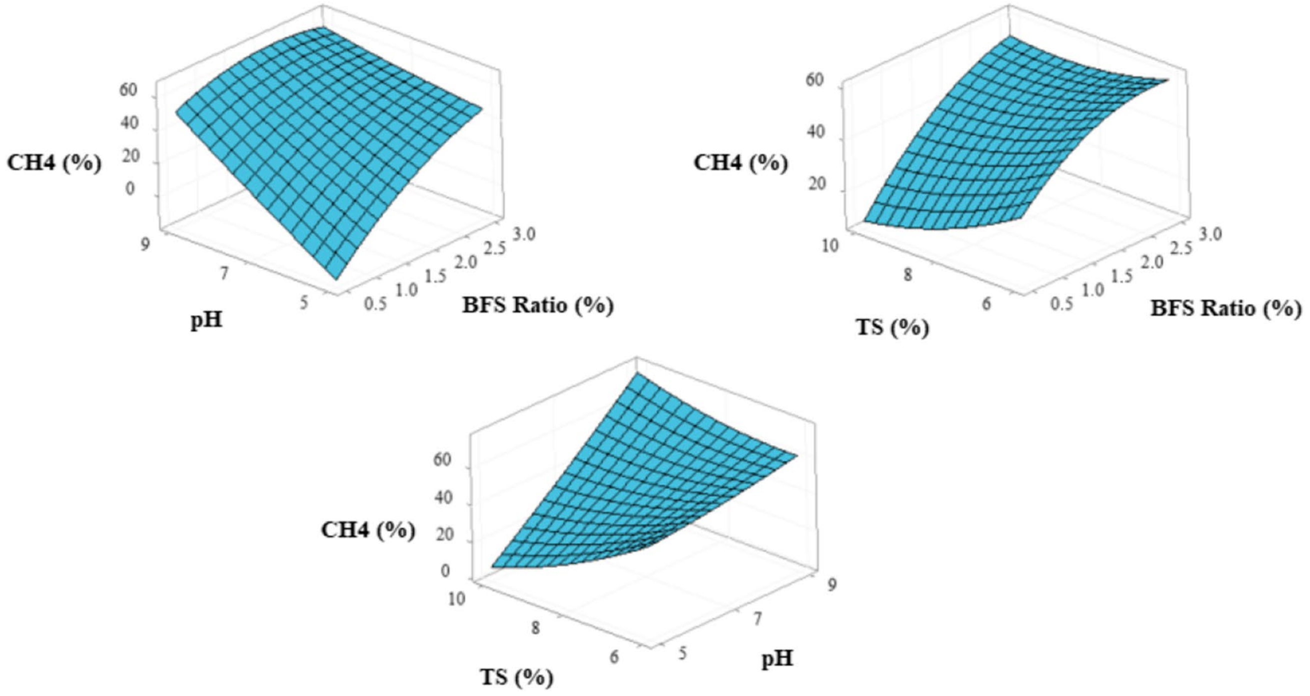


Fig. 7 Response surface plots of CH_4

observed that the cumulative biogas production increases due to the increase in the BFS ratio and the TS besides the initial pH. This can be described as follows: increase in initial TS increases biogas production because of the easily biodegradable substances [29]. Furthermore, BFS is an additive including metal oxides and adding metal oxide additives to AD can enhance the direct interspecies electron transfer (DIET) between the microorganisms and increase biogas production on AD [43]. The change in biogas yield at different pH, TS, and BFS ratios is shown in Fig. 6. Biogas yield increased with the increasing pH and BFS ratio. The maximum biogas yield was achieved

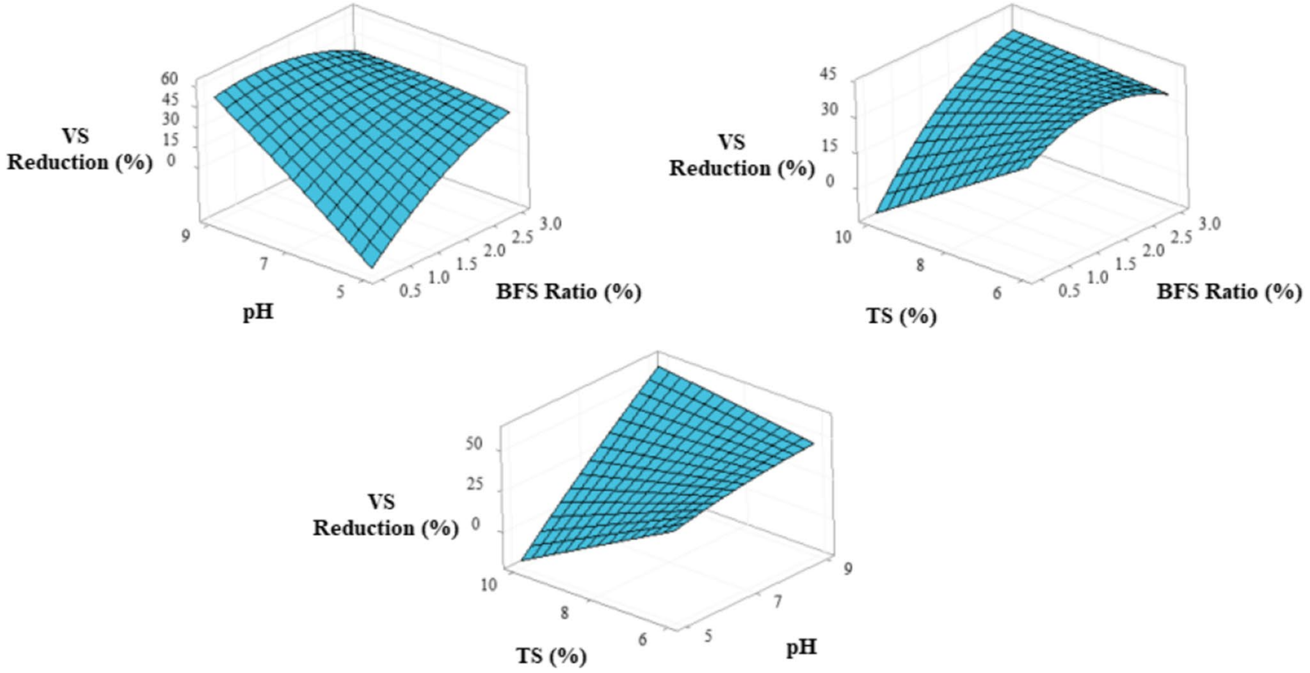


Fig. 8 Response surface plots of VS reduction

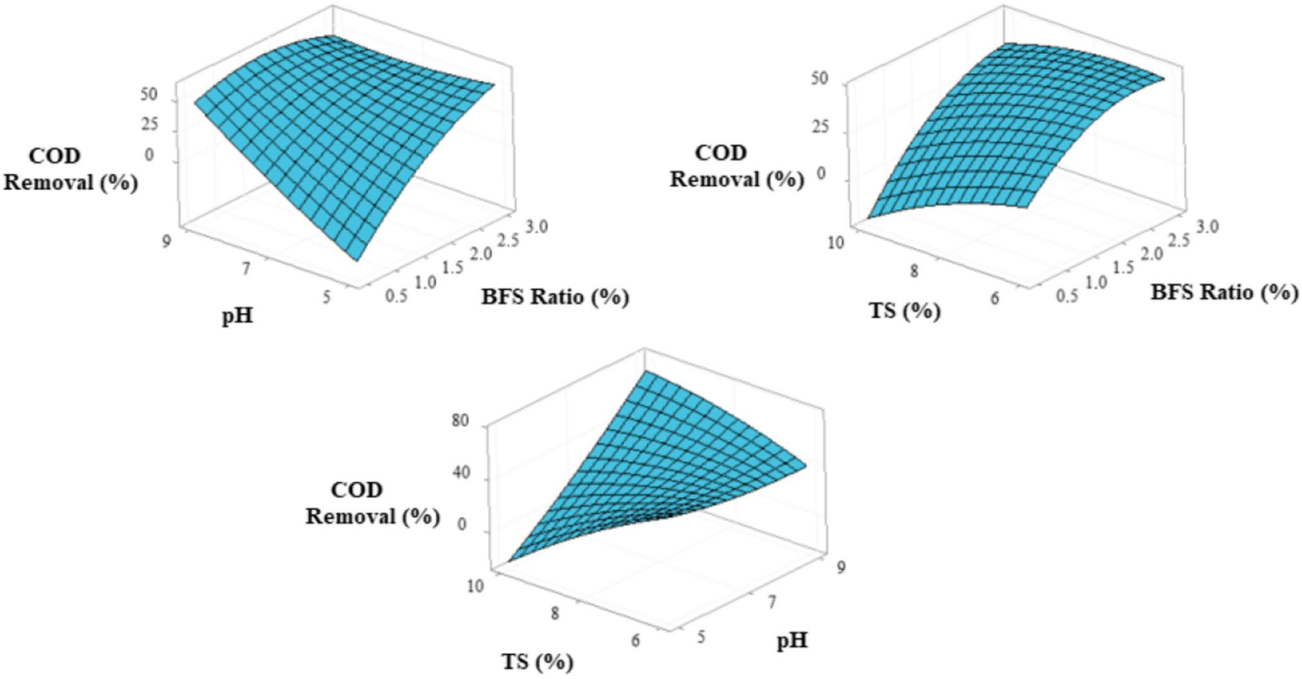
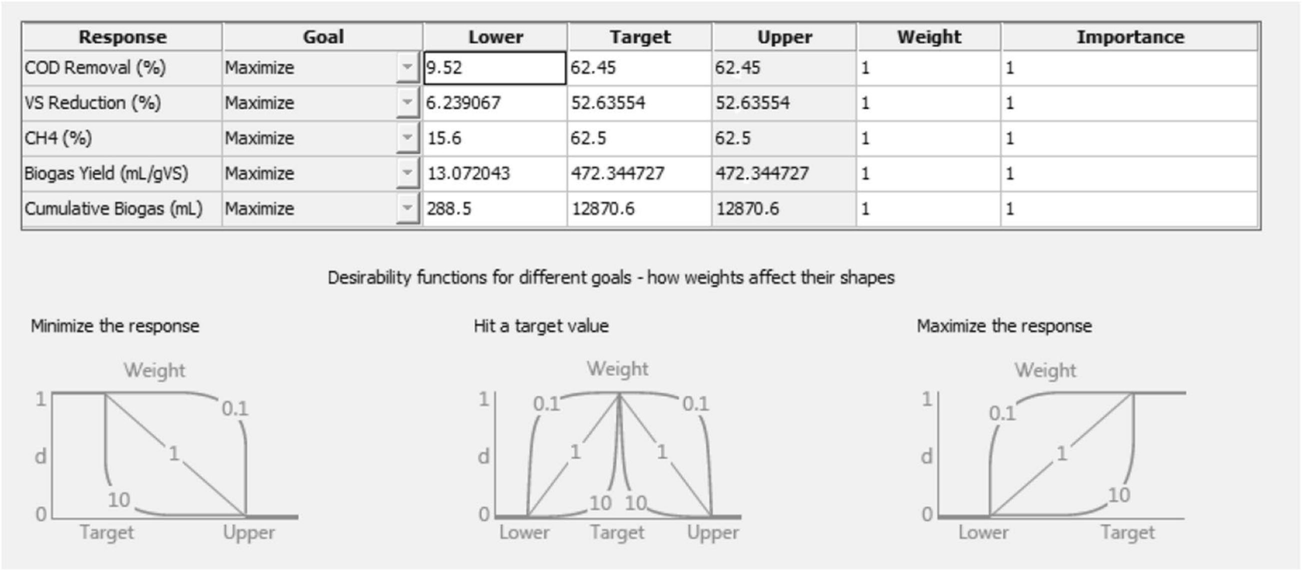


Fig. 9 Response surface plots of COD removal

at 9 pH and 1% BFS ratio. TS is the most effective parameter in the biogas yield and increasing TS ratio resulted an increase in biogas yield. Biogas yield is a calculable parameter and it highly depends on amount of biogas and TS ratio so results are very similar with cumulative biogas study. CH_4 production is based upon methanogenic activity on AD and also the operational conditions that suitable conditions for methanogens. Figure 7 shows response surface plots of CH_4. CH_4 increased with both increasing BFS ratio and pH. Before mentioned BFS adding on AD can positively affect the DIET and this can enhance the metabolic activity of methanogens. VS and COD is commonly used as an indicator of the amount of organic matter that can will be converted to biogas [29, 44]. Figure 8 and Fig. 9 show the simultaneous effects of selected responses on VS reduction and COD removal. As can be seen in both Fig. 8 and Fig. 9, all the plots are very similar because of



Response	Goal	Lower	Target	Upper	Weight	Importance
COD Removal (%)	Maximize	9.52	62.45	62.45	1	1
VS Reduction (%)	Maximize	6.239067	52.63554	52.63554	1	1
CH4 (%)	Maximize	15.6	62.5	62.5	1	1
Biogas Yield (mL/gVS)	Maximize	13.072043	472.344727	472.344727	1	1
Cumulative Biogas (mL)	Maximize	288.5	12870.6	12870.6	1	1

Desirability functions for different goals - how weights affect their shapes

Fig. 10 Optimization principles of RSM

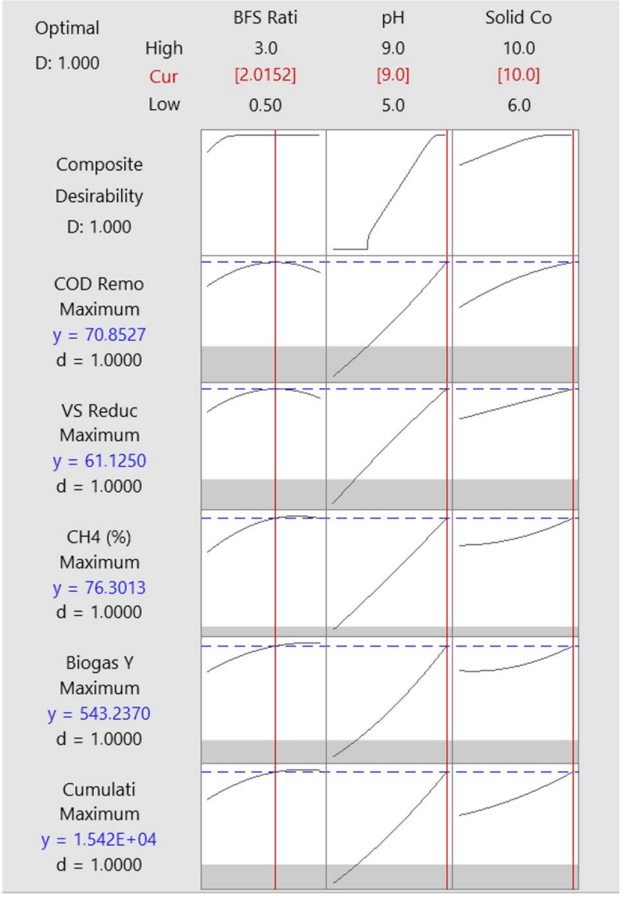


Fig. 11 Optimization plots for optimum conditions

VS removal also provides COD removal and all parameters affecting VS removal also effect COD removal.

3.3 Optimization studies

Finally, using the numerical optimization model in BB, optimization of the input parameters (BFS ratio, TS, and initial pH) was performed to obtain maximum values in the output parameters (cumulative biogas production, biogas yield, CH_4 content, VS reduction, and COD removal). Figure 10 shows the optimization principles of RSM. It has been tried to obtain maximum values in all output parameters.

The results of the optimization for maximum output values were obtained at 2.01%, 9, and 10% for BFS ratio, pH, and TS, respectively. Under these conditions, the highest cumulative biogas production was 15,420 mL, biogas efficiency was 543.23 mL/gVS, CH_4 76.30%, VS reduction 61.12%, and COD removal was 70.85% (Fig. 11).

4 Conclusions

This study focused on optimization of selected operational conditions on biogas production by using RSM. BFS ratio, TS, and pH were selected as input parameters for RSM and cumulative biogas, biogas yield, CH_4, VS reduction, and COD removal were selected as output parameters. High R^2 values (93.59–96.45%) obtained by ANOVA showed the RSM could be used for optimization of biogas production. Depending on the results of RSM, optimum conditions for the highest output values are obtained as 2.01%, 9, and 10% for BFS ratio, TS, and pH, respectively. Under these conditions, the maximum biogas production is 15420 mL, biogas yield 543.23 mL/gVS, and CH_4 76.30%. VS removal was 61.12% and COD removal was 70.85%. The results showed that RSM is a useful tool for optimization of biogas production by AD. Furthermore, results showed that using BFS can improve biogas production and it can be use as a additive on anaerobic digestion.

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