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Optimization of the Combined Effect of Selected Metals on Biogas Production from Cow dung

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ABSTRACT: The study utilized Response Surface Methodology (RSM) to optimize the concentrations of Cobalt, Iron, and Zinc for enhancing biogas production from cow dung. The highest biogas yield was observed at higher concentrations of cobalt and iron, with zinc also contributing positively but to a lesser extent. Cobalt significantly enhanced biogas yield and methane content at concentrations between 1.75 and 3.0 mg/L, consistent with its role as a cofactor for vitamin B_{12}. Iron improved biogas production by enhancing electron transfer and reducing the accumulation of volatile fatty acids (VFAs). The optimal concentration range for iron was 10–12.5 mg/L. Zinc showed a dual effect on biogas production, enhancing enzyme activity and microbial growth, leading to increased biogas yield. The model developed was found to be significant and adequately described the relationship between trace metal concentrations on biogas and methane production, particularly iron have a notable impact and cobalt shows strong influence and their combined interaction between iron and cobalt is particularly strong with the models demonstrating high predictive accuracy, emphasizing the importance of a balanced supplementation approach.. The optimal concentrations were determined to be 2.5 mg/L for cobalt, 12.5 mg/L for iron, and 3.5 mg/L for zinc. Under these optimized conditions, biogas yield increased by 32% compared to the control, reaching 135.2 g biogas yield in validation experiments. Further research and practical applications based on these results can contribute to the advancement of renewable energy technologies and sustainable waste management practices.

Keywords: Response Surface Methodology (RSM), Anaerobic Digestion, Trace Metals, Cow dung, Biogas Production

I. INTRODUCTION

The world's energy consumption is expected to double by 2035 due to the rapid growth in global energy demand [1]. As a result, energy experts have been searching for ways to sustainably meet the demand. Several studies have been conducted in the past century on the connections between development and energy. According to research, without modern energy, inclusive growth is not feasible [2]. Nigeria is now experiencing an electricity problem. The ongoing inability of Nigeria's government and power industry to supply both urban and rural populations with a sufficient quantity of electricity is known as the "energy supply crisis" in Nigeria. This is demonstrated by Nigeria's low electrification rate overall, which stands at 56.5% [3]. Peak generation capability is roughly 5300 MW, whereas the projected annual energy demand is 17,520 MW, but peak generation capability is around 5300 MW [4]. Petroleum and other fossil fuels are essential to the generation of energy and power in Nigeria's energy sector. According to the International Renewable Energy Agency (IRENA), renewable energy sources currently account for around 33% of the world's total electricity generation; however, in Nigeria is 18.2% [5], [6]. This exerts pressure on the limited renewable energy resources available as fossil fuel availability continues to deplete. Thus, the appeal for renewable energy sources has grown exponentially in the pursuit of climate change mitigation whilst still expanding energy access. Research has shown that solar and biomass have the most potential for energy generation in Nigeria, with 4 – 6.5 KWh/m2 of solar irradiation available per day and approximately 2.3 X 109 GJ bioenergy potential per year [7]. Most of the developing nations are facing serious shortage of fuel, the most commonly used fuel being wood fuel. The case in Nigeria is not different.

Biomasses are widely available, and their utilization for energy production has a great potential to reduce carbon dioxide (CO2) emissions and consequently to prevent global warming. Therefore, biomass helps not only the atmospheric CO2 recycling, but also contributes to the energy demands for the industrialized and developing countries worldwide. The most important biomass energy sources are wood, crops and their waste byproducts, municipal and animal solid wastes, food processing wastes, and aquatic plants and algae [8]. The agricultural sector produces 50–60% of total global methane emissions, and livestock production operations, particularly ruminants, are known as the primary source of this methane [9]. Bioenergy utilization has more attention in the last decade due to the massive depletion of fossil fuels that calls for an increased use of renewable energy resources [10]. Biogas production from organic waste, such as cow dung, has gained increasing attention as a sustainable and renewable source of energy. Cow dung, a readily available agricultural waste product, contains organic matter that can be anaerobically digested to produce biogas, primarily composed of methane (50-75%) and carbon dioxide (25-50%). However, the efficiency and quality of biogas generation from cow dung can be influenced by various factors, including feedstock composition, microbial activity, and environmental conditions. Cow dung (CD) contains a considerable amount of methanogenic bacteria but low amounts of cellulose, lignocelluloses, lignin and other organic components which are essential for bacterial growth and for biogas production. It also contains some different minerals like nitrogen, potassium, along with trace amounts of Sulphur, iron, zinc, copper, cobalt and manganese, etc. [11].

Organic matter can naturally decompose and degrade into its simpler chemical components through a process called anaerobic digestion, which occurs in the absence of oxygen. Anaerobic microorganisms digest the organic materials, in the absence of oxygen to produce methane and carbon dioxide as end products under ideal conditions [12], [13]. Anaerobic digestion is widely accepted as a source of renewable energy. In anaerobic digestion, biodegradable material is broken down by microorganisms without the presence of oxygen through a step-by-step process. The steps involved in creating biogas are broken down into four categories. Each step is mediated by specific groups of microorganisms that break down complex organic compounds into simpler molecules, ultimately producing methane (CH_4) and carbon dioxide (CO_2) [14]. All four of these phases must exist simultaneously to sustain a stable anaerobic process. The energy carrier in biogas is methane and it is produced during the methanogenesis stage, the full process of anaerobic digestion occurs in the following four stages [15], [16]; Hydrolysis, in which complex molecules are broken down to constituent monomers, Acidogenesis, in which acids are formed, Acetogenesis, or the production of acetate, and Methanogenesis, the stage in which methane is produced from either acetate or hydrogen. The digestion is not complete until the substrate undergone all of these stages, each of which has a physiologically unique bacteria population responsible, that requires distinct environmental conditions.

Several conditions and variables must be applied to obtain a proper breakdown of the organic compounds. The rate at which the microorganisms grow is of paramount importance in the anaerobic digestion process. Controlling the digester's operational parameters is necessary to enhance microbial activity and improve the system's anaerobic degradation efficiency. To optimize the process, many critical parameters related to anaerobic digestion must be controlled like Temperature, pH, Total Solid, hydraulic retention time, and nutrients.

In recent years, there has been a growing interest in the optimization of biogas production from various organic waste materials. One particular area of focus has been the role of metals as additives to enhance the performance and stability of the biogas production process. Several studies have shed light on the complex relationship between different metals and their impact on biogas yield with varying result. The performance and stability of biogas digesters, particularly when operated with animal manure, are significantly affected by the presence of heavy metals. These metals act as biostimulants for the methanogenic bacteria responsible for the anaerobic digestion process, leading to an increase in biogas and methane production. The presence of metals in animal dung can positively impact biogas production by improving the overall performance of anaerobic digestion. Studies have shown that the availability of heavy metals significantly affects the performance and stability of biogas digesters when operated with animal manure. The concentrations of heavy metals present in organic waste, as well as animal manure and industrial wastewaters, can have varied effects on the biochemical reactions involved in biogas production. Depending on their concentration, heavy metals can influence biochemical reactions in stimulatory, inhibitory, or even toxic, depending on their concentrations [17]. It has been observed that adding metal ions to anaerobic digesters significantly impacts the system's performance. While many enzymes and coenzymes in anaerobic digestion depend on certain heavy metals, like Ni, Co, Zn, and Cu, at low concentrations for activation or proper functioning, large concentrations of these metals can be toxic or inhibiting [18]. Nutrients and trace elements play crucial roles in the enzymatic activities and growth of microorganisms involved in anaerobic digestion has been extensively studied, particularly their significance as enzymatic cofactors. They act as cofactors for enzymes, influence microbial metabolism, and affect the overall stability of the digestion process [19]. These metals are needed in trace amounts to ensure optimal microbial activity and biogas production.

According to reports, the primary light metals influencing the anaerobic digestion process are sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and aluminum (Al). These metals are required in the process for the microbial growth, enhancement of the bacterial cell immobilization (Ca), and formation of adenosine phosphate (Na^+). However, the concentrations of these light metals should be controlled where: Mg^{2+} is responsible for limiting the production of double cells, K^+ is in charge of neutralizing the cell membrane potential, Na^+ can inhibit the acetoclastic methanogens, Ca^{2+} is accountable for the destabilization of the buffering system through precipitation of phosphates and carbonates also demonstrated to be necessary for the breakdown of cellulose, and finally, Al^{3+} is considered as an inhibitor of the anaerobic process—it can also compete with the adsorption of other metals. The heavy metals affecting the anaerobic digestion are mainly iron (Fe), copper (Cu), zinc (Zn), nickel (Ni), cobalt (Co), molybdenum (Mo), chromium (Cr), cadmium (Cd), lead (Pb), and mercury (Hg), the inhibitory and optimum metals concentrations can vary for different temperature conditions of the digesters. [19], [20]. It is important to note that not all heavy metals have the same effect on biogas production. The concentration and interplay of various heavy metals in animal dung can have differential effects on the anaerobic digestion process. Therefore, it is essential to carefully monitor and control metal concentrations in biogas production to ensure optimal performance and safety [18]. Notably, the specific effects of nickel and cobalt are stimulatory at certain concentration ranges, positively impacting biogas yield. In addition, the complex biomethanation process is facilitated by metals like iron, nickel, and cobalt, which play crucial roles at different stages of anaerobic digestion. For example, nickel has been observed to decrease the percentage of dihydrogen in biogas during the acidogenesis phase, while iron has been found to have the opposite effect, increasing the percentage. These metals facilitate the conversion of organic matter into methane by enhancing the activity of methanogenic bacteria [19], [20].

One promising avenue is the production of biogas through anaerobic digestion, a process that harnesses organic waste materials such as cow dung to generate methane-rich gas. However, the efficient and reliable production of biogas from cow dung presents a multifaceted challenge, like the digestion process, which includes metal concentration, temperature, pH levels, and residence time, which is crucial for maximizing biogas production. Inconsistencies in these variables can lead to suboptimal digestion and reduced biogas yields. Thus, this gap hinders the ability to maximize the potential of cow dung as a reliable and efficient source of biogas. To address the foreseen challenges, it is imperative to investigate means that will enhance and optimize the generation of this gas by optimizing the concentration of metals in the anaerobic digestion of cow dung. This study aims to optimize the combined effect of selected metals on biogas production from cow dung using response surface methodology central composite design (CCD).

II. MATERIALS AND METHODS

The materials employed in this research work are thus presented:

i. Cow dung
ii. Selected metals (Cobalt, Iron and zinc ion)
iii. Plastic bottles (750 ml), conical flask (250ml), measuring cylinder (500 and 1000 ml) and displacement tank
iv. Gas bag (500 ml)
v. Water, mortar and pestle, corks, valves and connecting tubes/ hose
vi. Design Expert software for RSM (Version 11.12.0) created by Stat-ease Incorporated.

A. Substrate Collection

The fresh cow dung was collected from Tudun Wada Zango Abattoir feedlot and stored in airtight containers to prevent contamination and loss of moisture. Since the fresh cow dung contains active methanogenic bacteria that will enhance gas production. The collected cow dung was screened by getting rid of foreign materials, such as stones and plastic, which cannot be decomposed easily or completely in the shortest possible time.

B. Substrate Preparation

The collected cow dung was mixed with water to achieve a suitable solids content (e.g. 10% w/v), which was then homogenized to ensure uniformity. This step provides a consistent substrate for experimentation. The ratio of slurry to water in the sample prepared was kept at a ratio 2:1 (w/w), cow dung to water, as a favourable ratio for adequate activity of bacteria for easy digestibility and gas production in the shortest possible time. Too much water makes the condition unfavorable for bacteria activity and growth. The mixture was then allowed for few minutes to stabilize.

C. Characterization of the substrate

The cow dung was characterized for its physicochemical properties. Total solids (TS) and volatile solids (VS) content were determined using the American Public Health Association (APHA) 2012 standard methods. The Total carbon and nitrogen content were analyzed to determine the C/N ratio. Background concentrations of Cobalt, Iron, and Zinc in the cow dung were determined using inductively coupled plasma mass spectrometry (ICP-MS) X-ray Fluorescent (XRF) analysis.

D. Trace Metal Solutions

Metals used in the experiments were laboratory-grade chemicals and analyzed by atomic absorption spectroscopy. Stock solutions of cobalt, iron, and zinc are prepared by dissolving cobalt chloride ($CoCl_2$), ferric chloride ($FeCl_2$), and zinc chloride ($ZnCl_2$) in distilled water, for each metal, a 1000 mL stock solution was prepared. These solutions were added to the cow dung substrate in specific concentrations as per the experimental design.

The trace metals cobalt (Co), iron (Fe), and zinc (Zn) were added to the anaerobic digestion process in the form of their respective salts: Cobalt chloride ($CoCl_2 \cdot 6H_2O$) , Ferric chloride ($FeCl_3 \cdot 6\ H_2O$) and Zinc chloride ($ZnCl_2$). These salts were chosen due to their high solubility in water and common use in similar studies.

E. Experimental Design

The experimental design is based on the Central Composite Design (CCD) of Response Surface Methodology (RSM). CCD is chosen for its efficiency in exploring the interactions between multiple variables and identifying optimal conditions. The three independent variables in this study are the concentrations of cobalt, iron, and zinc. The design includes factorial points, axial points, and center points to capture a wide range of conditions and interactions.

i. Experimental Runs

For this study, the independent variables were the concentrations of cobalt (Co), iron (Fe), and zinc (Zn). The dependent variable was the biogas yield. Each metal was tested at five levels (-α, -1, 0, +1, +α) Where α is the axial distance from the center point, and the CCD was used to generate 20 experimental runs, including 8 factorial points, 6 axial points, and 6 center points. The observed biogas yields are recorded and used for statistical analysis.

Table 1: Independent Variables and Their Levels

Variable	Symbol	-1 Level (Low)	0 Level (Center)	+1 Level (High)
Cobalt	Co	0.5 mg/L	1.75 mg/L	3 mg/L
Iron	Fe	5 mg/L	10 mg/L	15 mg/L
Zinc	Zn	1 mg/L	3 mg/L	5 mg/L

ii. Experimental Setup

Each experimental run was conducted in 750 mL laboratory-scale anaerobic digesters. The digesters were filled with 500 mL of cow dung substrate and inoculum slurry (10% total solids) and the respective concentrations of cobalt, iron, and zinc. The bio-digesters were sealed to ensure anaerobic conditions and equipped with a gas collection system to measure the volume of biogas produced.

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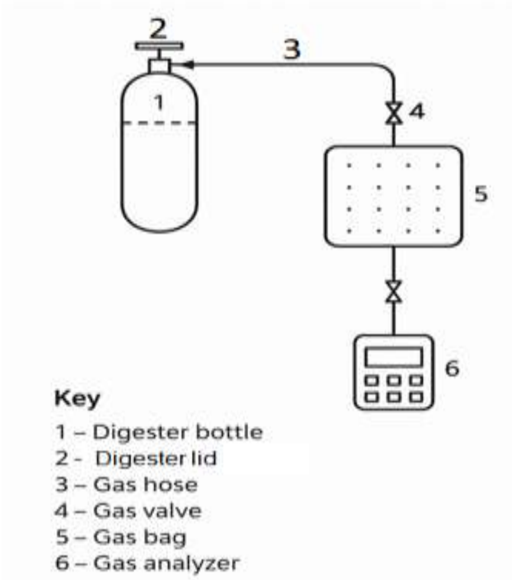

Fig. 1: The Experimental Layout

F.
Experimental Procedure

i. Digester Loading: After ensuring an adequate homogeneous mixture, the slurry prepared (mixture of cow dung substrate and inoculum in a 1:1 ratio on a wet weight basis) was then passed through a funnel into the various digester bottles. Adequate volume was introduced into the digester and labeled.

ii. Trace Metals Supplements: Trace metal solutions were added to the reactors according to the CCD design matrix to study their combined effects on biogas production. Addition of metals was done after the digesters were filled with the substrate and inoculum, but before sealing, to ensure proper mixing.

iii. Mixing Procedure: After adding the trace metal solutions, each digester was gently swirled for 1 minute to ensure homogeneous distribution of the metal. Care was taken to avoid excessive agitation that could introduce oxygen into the system.

iv. pH values were adjusted to the optimal level range for methanogenesis (pH 6 - 7)

v. Anaerobic Conditions: The digesters were purged with N2 gas, sealed to maintain anaerobic conditions and incubated at a mesophilic temperature range for digestion (20 - 45°C) and a hydraulic retention time of 30 days to ensure maximum gas production. The bio-digesters were agitated manually on daily basis prior to the reading of biogas production.

vi. Control Experiments: Control digesters without added trace metals were included in the experimental batch to serve as a baseline for comparison.

vii. Monitoring and Measurement: The total biogas production was measured using the water displacement and weighing method (gas bags). The methane content of the biogas was analyzed using gas chromatography (GC). The biogas produced in bio-digester accumulates in the headspace and built-up pressure which was the driving force for the displacement of water in the gas collecting system, and the amount of water displaced is equivalent to the biogas produced.

G. Statistical Analysis

Design of experiment (DOE) is a well-accepted statistical technique able to design and optimize the experimental process that involves choosing the optimal experimental design and estimate the effect of the several variables independently and also the interactions simultaneously [21].

The experimental data were analyzed using the Design-Expert software package created by Stat-ease Inc (version 11.12.0). The software was used for the design of the experiment (DOE) and optimization of variables and to fit a quadratic

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polynomial model to the data and to perform analysis of variance (ANOVA) to assess the significance of the model based on $p<0.05$ and the individual factors, the graphical tools help identify their impact on the outcomes.

H. Response Surface Methodology (RSM) Analysis

RSM was employed to develop a predictive model for biogas production. The model includes linear, quadratic, and interaction terms for the three metals. The general form of the quadratic polynomial model is:

$$Y = \beta^0 + \Sigma\beta_i x_i + \Sigma\beta_{ii} x_i^2 + \Sigma\Sigma\beta_{ij} x_i x_j + \varepsilon$$

Where: Y is the predicted response (biogas yield), βo is the intercept term, β_i are the linear coefficients, β_{ii} are the quadratic coefficients, β_{ij} are interaction coefficients, Xi and Xj are the independent variables (trace metal concentrations), and ε is the random error.

In this study, the independent variables were coded as A, B and C. Thus, the second-order polynomial equation can be represented as:

i. The factors (independent variables) are: A: Cobalt concentration (mg/L), B: Iron concentration (mg/L) and C: Zinc concentration (mg/L)
ii. The response (dependent variable) is: Y: Biogas yield (mL/g)

$$Y = \beta o + \beta 1A + \beta 2B + \beta 3C + \beta 11A2 + \beta 22B2 + \beta 33C2 + \beta 12AB + \beta 23BC + \beta 13AC$$

Response Surface Analysis: Diagnostics 3D surface Plots, 2D contour plots and model graphs were obtained using the Stat-Ease software with Design Expert v.11.12.0 to analyze and visualize the effects of variables and their interactions to determine their optimum level. The point prediction method was used for optimization of the levels of each variable for maximum response.

III. RESULTS AND DISCUSSION

A. Characterization of Cow Dung

The physicochemical properties obtained are presented in Table 2. The table indicates that the cow dung has an average dry matter of 72.7% with a volatile matter of 46.4%. The average moisture content, pH value and C/N ratio of the cow dung was found to be 27.3%, 6.8 and 22.97 respectively.

Table 2: Physicochemical characteristics of cow dung

S/N	Parameter	Value
1	Moisture Content	27.3 ± 0.5 %
2	Dry Matter	72.7 ± 0.3 %
3	Ash Content	1.03 ± 0.5 %
4	Volatile Matter	46.4 ± 0.2 %
5	Fixed Carbon	25.27 ± 0.5 %
6	pH	6.8 ± 0.1
7	C/N ratio	22.97 ± 0.5
8	Carbon	78.3 ± 0.3 %
9	Hydrogen	2.09 ± 0.1 %
10	Nitrogen	12.23 ± 0.5 %
11	Oxygen	6.37 ± 0.2 %
12	Sulphur	1.01 ± 0.2 %
13	Background Co concentration	0.007 %
14	Background Fe concentration	1.338 %
15	Background Zn concentration	0.029 %

The cow dung exhibited characteristics typical of bovine manure, with a C/N ratio within the optimal range for anaerobic digestion, and found similar to those in the literature. The background concentrations of trace metals were relatively low, particularly for Cobalt, suggesting potential for improvement through supplementation.

B. Biogas Production Data

The obtained biogas production data for the various combinations of cobalt, iron, and zinc concentrations are presented in Table 3. The results show that biogas yield is significantly influenced by the supplementation of the trace metals.

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Table 3: Design of experiments and their corresponding experimental results

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A:cobalt	B:Iron	C:Zinc	Biogas Yield
		mg/l	mg/l	mg/l	g
19	1	1.75	10	3	131
13	2	1.75	10	-0.363586	118
20	3	1.75	10	3	131.5
2	4	3	5	1	96
8	5	3	15	5	124
1	6	0.5	5	1	102
4	7	3	15	1	133
15	8	1.75	10	3	130.5
11	9	1.75	1.59104	3	106
18	10	1.75	10	3	134
12	11	1.75	18.409	3	129.5
17	12	1.75	10	3	111
10	13	3.85224	10	3	124
14	14	1.75	10	6.36359	121
6	15	3	5	5	100.5
16	16	1.75	10	3	131.5
5	17	0.5	5	5	101
3	18	0.5	15	1	105.5
7	19	0.5	15	5	106.5
9	20	-0.352241	10	3	103

Key Response Discussion

i. **Biogas Yield:**

Highest yield (134 g) was obtained when all three variables are balanced (moderate-to-high cobalt, iron and zinc). Lower yields (96 g) occurred when two variables (like iron and zinc) are at low concentrations, limiting microbial activity and Mean yields: 116.97 g. Center point consistency: Runs 1, 3, 8, 10, 12, 16 show average good yield, indicating stable performance at mid-range conditions, suggesting a synergistic effect between these metals.

ii. **Extremes Effects**:

Low cobalt (-0.35 mg/L, Run 20) resulted in low biogas (103g) and High zinc (6.36 mg/L, Run 14) gave moderate biogas (121g).

Table 4: Control experimental results without trace metals supplement

Sludge (g)	Biogas (g)	Biogas (%) = [Biogas (g)*100]/ Sludge (g)
500	103	20.6

The control experiment result without trace metal supplement indicates a low biogas yield (103 g) below the average result of the metals supplemented experiment; biogas yield (116.97 g) which validates the enhancement of biogas production.

C. Response Surface Analysis

i. **Model Fitting**

The obtained response surface model for biogas yield and methane content was fitted to a quadratic polynomial equation:

$$\mathbf{Y1 = 128.5 + 5.41A + 7.98B + 0.0399C - 6.83A^2 - 5.33B^2 - 4.71C^2 + 6.44AB - 0.5625AC - 1.44BC}$$

Iron (B) has the strongest positive effect followed by Cobalt, cobalt and Iron (AB) interaction boost yield and negative coefficient for Cobalt (A^2), Iron (B^2) and Zinc (C^2) indicate curvature (optima exist within the range).

Where Y_1 is the predicted biogas yield (g), and A, B, and C are the coded values for Cobalt, Iron, and Zinc concentrations, respectively.

D. Analysis of Variance (ANOVA)

The results of ANOVA are presented in Table 6.

Table 6: ANOVA for Response Surface Quadratic Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	2799.23	9	311.03	5.14	0.0087	significant
A-cobalt	399.00	1	399.00	6.59	0.0280	
B-Iron	870.32	1	870.32	14.37	0.0035	
C-Zinc	0.0218	1	0.0218	0.0004	0.9852	
AB	331.53	1	331.53	5.48	0.0413	
AC	2.53	1	2.53	0.0418	0.8421	
BC	16.53	1	16.53	0.2730	0.6127	
A^2	672.82	1	672.82	11.11	0.0076	
B^2	409.43	1	409.43	6.76	0.0265	
C^2	319.90	1	319.90	5.28	0.0444	
Residual	605.51	10	60.55			
Lack of Fit	241.13	5	48.23	0.6618	0.6692	not significant
Pure Error	364.38	5	72.88			
Cor Total	3404.74	19				

The analysis of variance (ANOVA) for the quadratic model is shown in Table 4.4 the **Model F-value** of 5.14 implies the model is significant. There is only a 0.87% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, AB, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 0.66 implies the Lack of Fit is not significant relative to the pure error. There is a 66.92% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Cobalt and Iron have a significant positive effect on biogas yield (p-value < 0.05) while Zinc has a non-significant effect on biogas yield (p-value > 0.05). The interaction between cobalt and iron is significant (p-value < 0.05)

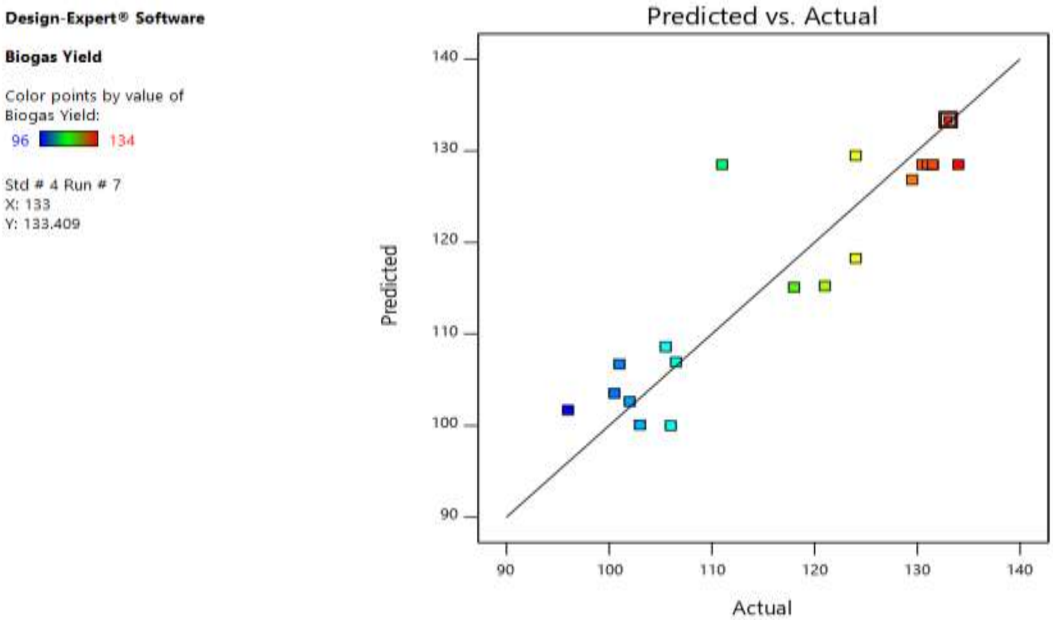

Fig. 2: Predicted vs Actual Plot for Biogas Yield

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The graph compares predicted biogas yield (modeled values) to actual experimental results. The highlighted point (Actual (X): 133 versus Predicted (Y): 133.409) shows minimal error (~0.4%), the close match suggested that the model predicts the observation well. The points are colored based on biogas yield values, ranging from 96 to 134 (blue/lower to red/higher). The diagonal line represents perfect prediction (Actual = Predicted). Points near this line indicate good model accuracy

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D. Interaction Effects of Trace Metals

The Interaction effects occur when the impact of one independent variable on the response depends on the level of another independent variable. In anaerobic digestion, these interactions are crucial as trace metals influence microbial metabolism through complex biochemical mechanisms. The interaction between cobalt, iron, and zinc is analyzed using response surface plots (Figures 3). The results show that the combined effect of these trace metals is more significant than their individual effects.

ii. Cobalt and Iron Interaction Effect

Figure 3a: The 3D surface response plot showing the effect of cobalt and iron on biogas yield. Cobalt and Iron have a strong interaction effect; the optimal conditions appeared to be around 1.75 mg/L cobalt and 10 mg/L iron, with zinc fixed at 3 mg/L. The 3D response surface confirms a peak yield of approximately 134g and the design point (marked with a circle) shows a measured yield of 130.5g in run #8 and 134g in run #10. At low cobalt levels (0.5 mg/l), increasing iron shows minimal impact, at high cobalt levels (3 mg/l), iron concentration dramatically increases biogas yield and Maximum synergistic effect observed at 1.75 mg/l cobalt and 10 mg/l iron, indicating that these metals work together to enhance microbial activity.

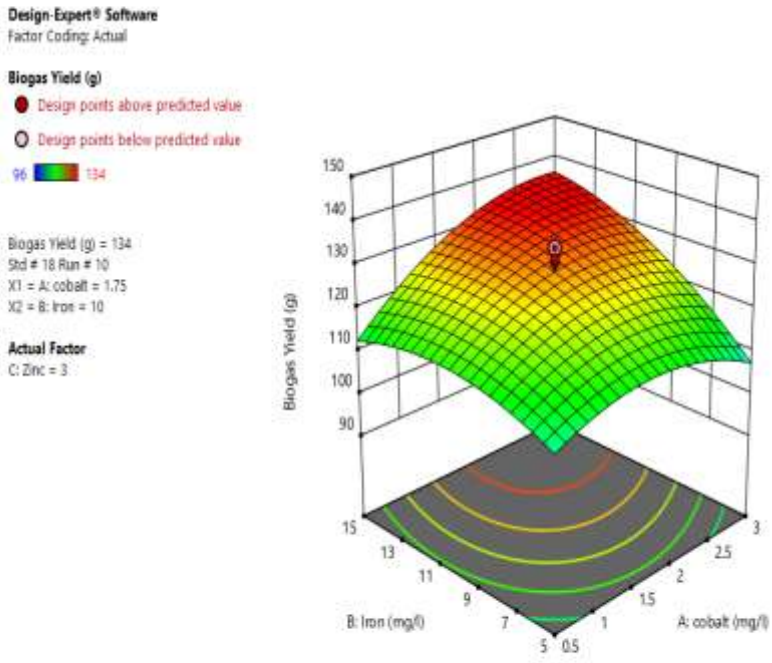

Fig. 3: Response Surface Plots (3D plot): (a) Effect of Cobalt and Iron on Biogas Yield

iii. Cobalt and Zinc Interaction Effect

Figure 3b: 3D surface response plot showing the effect of cobalt and zinc on biogas yield. Cobalt and Zinc have a moderate interaction effect; the optimal conditions appeared to be around 1.75 mg/L cobalt and 3 mg/L zinc, with iron fixed at 10 mg/L. The 3D response surface confirms a peak yield of approximately 134g and the design point (marked with a circle) shows a measured yield of 130.5g in run #8 and 134g in run #10, suggesting instability, and Zinc = 3 mg/l: More consistent high yields (~120–134 g), indicating a stabilizing effect.

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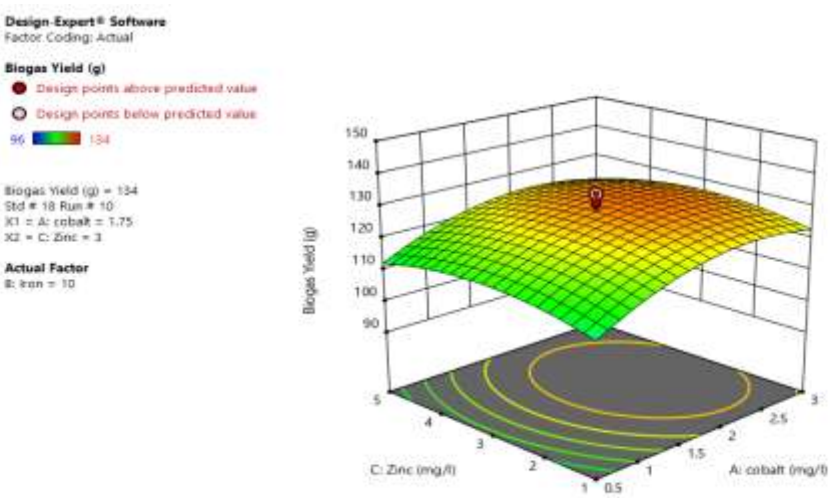

Fig. 3: Response Surface Plots (3D plot): (b) Effect of Cobalt and Zinc on Biogas Yield

iv. Iron and Zinc Interaction Effect

Fig. 3c: 3D surface response plot showing the effect of iron and zinc on biogas yield. Iron and Zinc have a moderate interaction effect; the optimal biogas yield appears to occur at approximately 11-13 mg/L iron and 3 mg/L zinc, with cobalt fixed at 1.75 mg/L. The 3D response surface confirms a peak yield of approximately 134g and the design point (marked with a circle) shows a measured yield of 130.5g in run #8 and 134g in run #10, higher iron concentrations (>10 mg/L) combined with moderate zinc levels (2-4 mg/L) create the most favorable conditions.

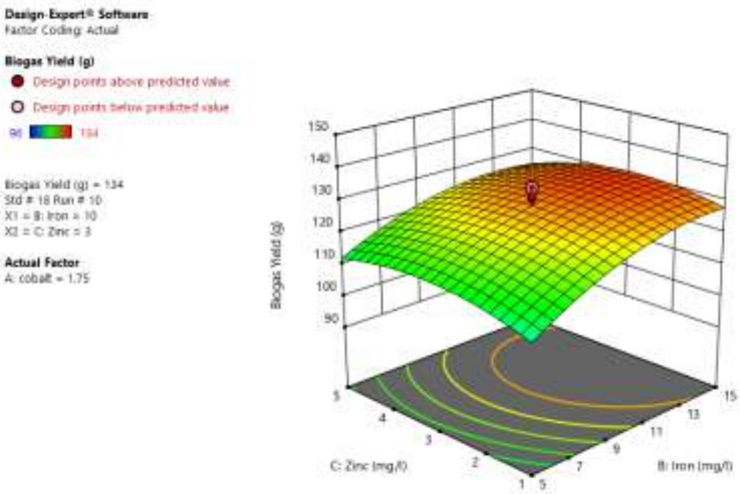

Fig. 3: Response Surface Plots (3D plot): (c) Effect of Iron and Zinc on Biogas Yield

E. Optimization of Metal Concentrations

The optimal concentrations of cobalt, iron, and zinc for maximizing biogas yield are determined using the desirability function in response surface model. The optimal combination of cobalt and Iron is around 2-3 mg/L and 10-15 mg/L, respectively. Increasing Cobalt and Iron concentrations beyond these levels does not significantly improve biogas yield. The recommended optimal conditions are: Cobalt 2.5 mg/L, Iron 12.5 mg/L and Zinc 3.5 mg/L. At these optimal conditions, the model predicted a maximum biogas yield of 135.7 g, representing a 32% increase on biogas yield over the control experiment.

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Table 4.8: Validation Experiments Result

Run	Factor 1 A:Cobalt mg/L	Factor 2 B:Iron mg/L	Factor 3 C:Zinc mg/L	Response 1 Biogas Yield g	Response 1 Biogas Yield %
1	2.5	12.5	3.5	134.9	26.98
2	2.5	12.5	3.5	135.6	27.12

The average biogas yield obtained was 135.2 g which is in close agreement with the model prediction (135.7 g). This result validates the accuracy of the RSM model and confirms the effectiveness of the optimization process.

IV. CONCLUSION

The study revealed significant interactions between the trace metals, highlighting the importance of a balanced supplementation approach. Strong synergies were observed between cobalt and iron at optimal concentrations resulted in a synergistic effect, enhancing both biogas yield and methane content. Zinc interacted negatively with cobalt and iron at higher concentrations, leading to reduced biogas production. This highlights the importance of balancing trace metal concentrations to avoid inhibition. The control experimental result without trace metal supplement indicate a low biogas yield (103 g) below the average result of the metals supplemented experiment; biogas yield (116.97 g) which validates the positive impact of trace metals on biogas production. The optimal concentrations determined were 2.5 mg/L for cobalt, 12.5 mg/L for iron, and 3.5 mg/L for zinc. Under these conditions, biogas yield increased by 32%, reaching 135.2 g, as confirmed by validation experiments. The close agreement between model predictions and experimental results validates the robustness of the optimization process and confirms the practical applicability of the findings for enhanced biogas production systems.

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