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THE EXTRACTION AND ABSORPTION OF HYDROGEN SULFIDE (H2S) FROM BIOGAS ALONG WITH THE PRODUCTION OF SULFUR, UTILIZING THE IRON CHELATE METHOD.

[1]Mr. Ajay Rana, [2]Mr. Nitin Harkar, [3]Ms.NishitaBhosale
[1]Mfg.Chemist, [2] Senior Consultant, [3]ESG Consultant
[1]Department of Chemistry,
[1]The Karnal Co-op Sugar Mills Ltd. Karnal

Abstract : Biogas is increasingly acknowledged as a sustainable and clean energy source generated from the anaerobic digestion of biodegradable organic materials. It is anticipated that biogas will play a significant role in replacing traditional energy sources. The primary components of biogas are methane (CH_4) and carbon dioxide (CO_2), along with various contaminants present in differing amounts, such as ammonia (NH_3), water vapor (H_2O), hydrogen sulfide (H_2S), methyl siloxanes, nitrogen (N_2), oxygen (O_2), halogenated volatile organic compounds (VOCs), carbon monoxide (CO), and hydrocarbons. Biogas is commonly used as fuel for engines or as a precursor for the production of chemicals, hydrogen, and synthesis gas. Certain applications necessitate a specific level of purity in biogas. The presence of trace contaminants can adversely impact engine performance, making the removal of impurities, particularly H_2S and CO_2, crucial for enhancing biogas quality and its effectiveness in various applications. Additionally, this removal process is essential to comply with established gas specifications for use as vehicle fuel or for injection into natural gas networks. Various methods for cleaning and upgrading biogas have been identified, each differing in functionality, efficiency, and the quality of input gas required. The extraction and absorption of hydrogen sulfide (H_2S) from biogas is crucial for enhancing the quality of this renewable energy source and mitigating environmental impacts. This study explores the utilization of the iron chelate method for effective H_2S removal and simultaneous sulfur production. The process involves the reaction of H_2S with iron chelates, leading to the formation of stable iron sulfides. Laboratory experiments demonstrate the efficiency of this method under varying conditions of temperature, pressure, and pH. The results indicate that the iron chelate method not only achieves high absorption rates of H_2S but also facilitates the conversion of H_2S into elemental sulfur, thus offering a dual benefit of waste reduction and resource recovery. Economic assessments suggest that the implementation of this method in biogas plants could enhance sustainability and profitability. This research highlights the potential of the iron chelate method as a viable solution for H_2S management in biogas utilization, contributing to cleaner energy production and sulfur recycling.

keywords **- Hydrogen sulfide (H2S) removal, Biogas purification, Waste minimization, Stable iron sulfides, Environmental impact.**

I. INTRODUCTION

Biogas is a renewable energy source that presents a viable alternative in terms of energy efficiency and environmental sustainability. It can be utilized for generating heat and electricity, and it can also be upgraded to biomethane for versatile applications. To convert biogas into biomethane, it is essential to undergo a purification process to eliminate harmful components. One of the most concerning trace impurities in biogas is hydrogen sulfide (H_2S), which poses significant challenges due to its corrosive effects on pipelines, compressors, gas storage tanks, and engines. Additionally, upon combustion, H2S transforms into even more corrosive substances, such as sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4).

Significant damage can occur in combustion equipment due to the presence of H_2S, making its removal a critical first step in the biogas purification process. A variety of methods have been developed for the extraction of H_2S from biogas, including liquid absorption, solid adsorption, biological degradation, and membrane separation, among others. Liquid absorption is a commonly employed desulfurization technique, where H_2S is chemically absorbed by various liquids such as sodium hydroxide, ferric chloride, and ferric hydroxide solutions, each operating through different reaction mechanisms. Notably, the catalytic oxidative absorption of

H2S using a chelated iron solution offers unique advantages over other liquid absorption methods. This approach converts H2S directly into elemental sulfur, which can be recovered for significant economic gain, and it also features a rapid reaction rate. Consequently, this desulfurization technique is often favored in numerous biogas utilization initiatives. The process of catalytic oxidative absorption desulfurization is outlined in Eqs. (1) to (5). In this method, H2S is dissolved in an aqueous scrubbing solution that contains ferric chelate.

($Fe3^{+}L$) (Eq. (1)), followed by two dissociation reactions (Eqs. (2) and (3)). HS produced in Eq. (2) is oxidized by Fe3 $^{+}$L in the solution to produce elemental sulfur (Eq. (4)). After separating the oxidation product of elemental sulfur, $Fe3^{+}L$ is regenerated through the re-oxidation of ferrous chelate ($Fe2^{+}L$) by air in the regenerator, and then it is used for oxidizing HS again. The regeneration reaction is described as Eq. (5). $Fe3^{+}L$ is the oxidizer in the desulfurization process. As it is regenerated during the circulations, it could also be considered as a catalyst of the process. In order to maintain a high H2S absorption rate, an alkaline solution is generally used for the scrubbing to neutralize the produced hydrogen ions (H^{+}) in Eq. (2) and make the reactions (1) and (2) shift to the right

H2S (gas) = H2S (aq) (1)
$H2S (aq) = H^{+} + HS^{-}$ (pKa = 7.0) (2)
$HS^{-} = S2^{+} + H^{+}$ (pKa = 12.9) (3)
$2Fe3^{+}L + HS^{-} = 2Fe2^{+}L + S\downarrow + H^{+}$ (4)
$4Fe2^{+}L + O2 + 2H^{+} = 4Fe3^{+}L + 2OH$ (5)
(where L represents chelant such as EDTA.)

In the process of catalytic oxidative desulfurization, the H^{+} ions generated in Equation (4) are counterbalanced by the OH $^{-}$ ions produced during the regeneration reaction (Equation (5)). Thus, theoretically, there is no need for extra alkali to sustain the pH of the scrubbing solution. However, biogas contains a significantly higher concentration of CO2 compared to H2S, which also dissolves in the desulfurization solution. The dissolved CO2 undergoes hydrolysis and dissociation in the solution, leading to the production of additional H^{+} ions (Equations (8) and (9)). This results in a gradual decline in the pH of the desulfurization solution. The reactions associated with CO2 absorption are detailed in Equations (6) to (9). As previously noted, a high pH in the scrubbing solution is essential for achieving an optimal H2S absorption rate, but the elevated CO2 concentration in biogas contributes to a decrease in pH. To ensure a high desulfurization efficiency, it is necessary to frequently add extra alkali, which incurs additional operational expenses.

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CO2 (gas) = CO2 (aq) (6)
CO2 (aq) + H2O = H2CO3 (7)
$H2CO3 = H^{+} + HCO_{3}$ (pKa = 6.4) (8)
$HCO3 = H^{+} + CO_{3}^{2-}$ (pKa = 10.3) (9)

To effectively lower operational costs, it is crucial to minimize CO2 absorption while maintaining desulfurization efficiency, as this can lead to reduced alkali consumption. The approach aimed at maximizing the absorption ratio of H2S to CO2, without significantly compromising desulfurization efficiency, is referred to as selective desulfurization. Desulfurization selectivity is characterized by the ratio of H2S absorbed to CO2 absorbed. The selective absorption of H2S over CO2 using amine solutions, such as mono-ethanolamine and N-methyldiethanolamine, as well as more complex formulations, has been extensively researched by various scholars. In recent years, studies have also explored selective H2S absorption through alternative alkaline scrubbing systems beyond amines. However, to our knowledge, there has been no reported research on the selectivity of biogas desulfurization utilizing a catalytic oxidative absorption method with chelated iron as the catalyst, despite its widespread application in many biogas processes. To effectively implement utilization projects, it is essential to comprehend the factors that affect the selectivity of H2S removal in comparison to CO2. This study aimed to evaluate the desulfurization selectivity of the catalytic oxidative absorption technique for biogas desulfurization. Experiments were conducted using a laboratory-scale setup, which included a gas scrubbing column and an air regenerator, with EDTA-Fe chosen as the desulfurization catalyst. The removal efficiencies for both H2S and CO2 were assessed under various experimental conditions. The selectivity factor, which indicates the selectivity of H2S removal in each scenario, was calculated. The impact of solution pH, chelated iron concentration, and the ratio of gas flow rate to liquid flow rate (G/L) on desulfurization selectivity was analyzed.

NEED OF THE STUDY.

The growing adoption of biogas as a renewable energy source has attracted considerable interest due to its ability to substitute conventional fossil fuels. Nonetheless, the presence of contaminants, especially hydrogen sulfide (H_2S), in biogas can impede its effective use and adversely affect the performance of engines, fuel cells, and other systems that demand high-quality, purified gas. H_2S is a hazardous and corrosive substance that can damage equipment, diminish energy production efficiency, and lead to environmental pollution if not adequately addressed. Purifying biogas is essential to ensure it complies with the quality standards required for its role as a clean energy source. Conventional techniques for H_2S removal from biogas include adsorption with solid media (such as activated carbon or iron oxide) and absorption through liquid scrubbing. However, these approaches often face challenges, including high operational expenses, reduced efficiency, and the generation of waste byproducts that necessitate further management. The iron chelate method offers a promising alternative. This technique not only effectively removes H_2S but also converts it into elemental sulfur, which can be utilized as a valuable byproduct in various industrial sectors. This dual-advantage approach has the potential to create a more sustainable and economically feasible solution for the management of H_2S in biogas facilities, harmonizing environmental objectives with financial factors. Consequently, it is essential to examine and enhance the iron chelate technique for H_2S extraction from biogas. This research intends to evaluate the effectiveness of this method across different conditions (temperature, pressure, pH) and to analyze its practicality regarding improvements in biogas quality, sulfur generation, and overall cost efficiency for biogas plant operations.

OBJECTIVES OF THE STUDY

i. Investigate the Effectiveness of the Iron Chelate Method for H_2S Removal.
ii. Assess Sulfur Production from H_2S.
iii. Evaluate the Environmental and Sustainability Impact.
iv. Economic Feasibility Assessment.

3.1 MATERIALS

Apparatus: Measuring cylinder, Beaker, Conical flask, Volumetric flask, Rubber tubes etc.
Reagents: di-sodium EDTA, Ferric chloride, Sodium carbonate (soda ash).
Instruments & Equipment 1) Tedlar bag 2) PH meter 3) Magnetic stirrer 4) Burner 5) Plastic container 6) Weighing machine.

3.2 Properties of Reagents

1. Disodium EDTA

Chelating Agent: Disodium EDTA serves as an effective chelating agent, creating stable, water-soluble complexes with various metal ions, including both FeZ^+ and $Fe3^+$.

Iron Availability: By preventing the precipitation of iron from the solution, EDTA ensures that iron remains accessible for reactions that eliminate H_2S.

Iron Regeneration: The compound facilitates the regeneration of iron by chelating sulfide ions, thereby releasing iron back into the solution for continued H_2S removal. pH Buffering: EDTA plays a vital role in maintaining a consistent pH, which is essential for the optimal functioning of iron chelates.

2. Ferric Chloride ($FeCl_3$)

Source: Ferric chloride serves as an accessible source of ferric iron ($Fe3^+$), the active form required to interact with and eliminate hydrogen sulfide (H_2S).

Reaction with H2S: When ferric iron encounters H_2S, it undergoes a reaction that produces iron sulfide (FeS) and elemental sulfur (S), thereby effectively reducing H_2S levels in biogas.

Solubility: Additionally, ferric chloride exhibits high solubility in water, allowing it to dissolve easily and supply ferric ions for the reaction.

3. Sodium Carbonate (Na_2CO_3)

pH Adjustment: Sodium carbonate is a basic salt used to adjust the pH of the solution. A slightly alkaline pH is generally optimal for iron chelate stability and H_2S removal efficiency.

Reaction with H_2S: Sodium carbonate can also directly react with H_2S to a limited extent, forming sodium sulfide (Na_2S) and sodium bicarbonate ($NaHCO_3$)

RESEARCH METHODOLOGY

The methodology section outline the plan and method that how the study is conducted. The details are as follows;

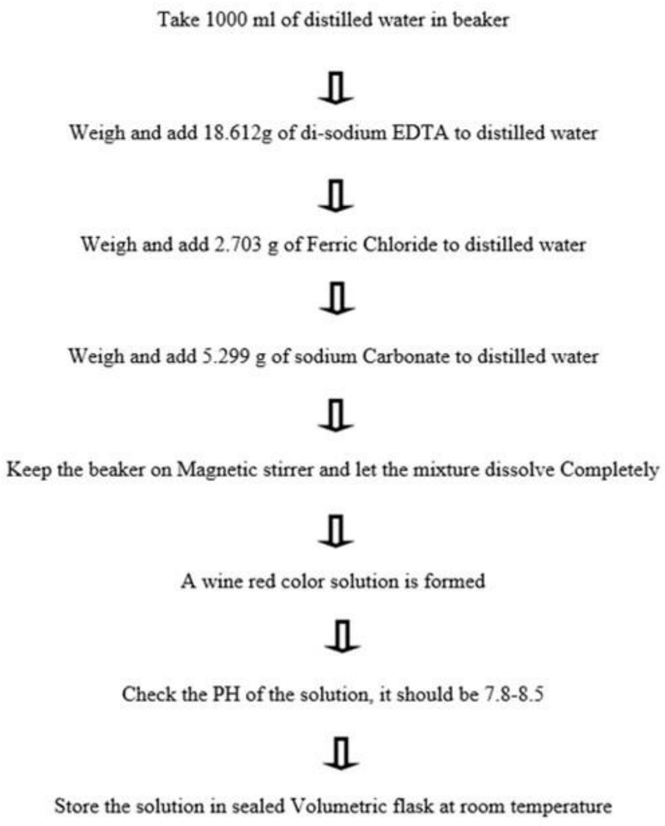
3.1 Preparation of ICS solution

- The ICS solution of 0.1 N was prepared using di-sodium EDTA, Ferric chloride, Sodium carbonate.
- To determine the concentration of chemical to prepare 0.1 N ICS solution Equivalent Weight is required.

The formula for Equivalent Weight is given below:
Equivalent weight = Molecular weight / N factor

Where, N = This represents the equivalence factor, which depends on the type of substance and its chemical behavior in a reaction. N factor is the total positive valency of metal ions in the salt.

- The concentration of each chemical required for 0.1 N ICS solution and the calculation performed to determine the amount of chemical required to prepare ICS solution are given below



Take 1000 ml of distilled water in beaker

Weigh and add 18.612g of di-sodium EDTA to distilled water

Weigh and add 2.703 g of Ferric Chloride to distilled water

Weigh and add 5.299 g of sodium Carbonate to distilled water

Keep the beaker on Magnetic stirrer and let the mixture dissolve Completely

A wine red color solution is formed

Check the PH of the solution, it should be 7.8-8.5

Store the solution in sealed Volumetric flask at room temperature

Figure 1. Flowchart of the procedure performed while preparing ICS solution

3.2 Experimental setup for desulphurization process

A plastic container of 2L capacity having an inlet at the bottom and outlet at the top was used.

Availability of sample: Raw biogas was extracted directly from Sampling outlet of the digester from Shreenath Mhaskoba sakhar karkhana ltd.

Gas Flow and pressure: The biogas was directed from the digester Sampling pipe into the inlet of the container at a pressure of 0.5 kg (shown in fig. 2), allowing it to bubble through the ICS solution for duration of 35 minutes. In this container the H2S is absorbed and transformed into sulfur.

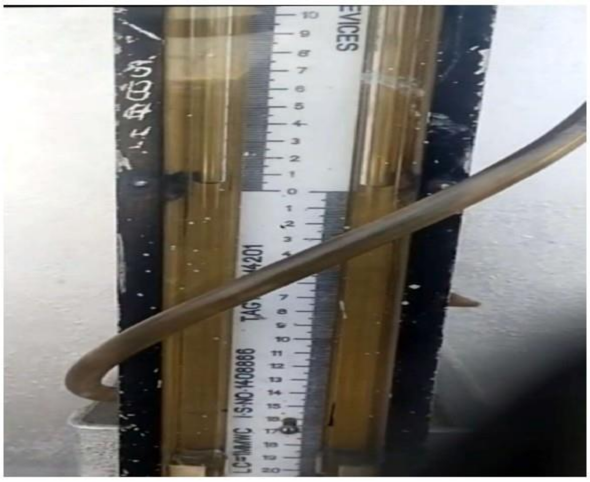


Figure 2. Pressure scale

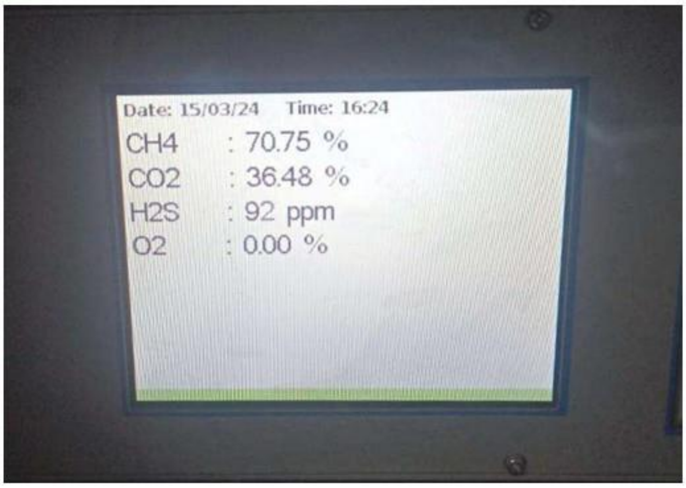
The solution from wine red to white, indicated the formation of sulfur.
The colour change of sulfur, signifying the removal of H2S from the biogas. (shown in Fig. 3)

Figure 3. Colour change of the solution indicating formation of sulfur

The desulphurized biogas exiting the container outlet was collected in Tedlar bag for subsequent analysis of H2S content.
The sulfur produced was easily recoverable from the solution by sedimentation in the container itself and filtration through whatman filter paper. (shown in Fig. 4).

Figure 4. Filtration of the sulfur from ICS solution

The composition of the outlet sample of biogas was determined by portable gas analyzer. (shown in Fig. 5).
H2S removal was expressed as PPM.



Date: 15/03/24 Time: 16:24

CH4 : 70.75 %
CO2 : 36.48 %
H2S : 92 ppm
O2 : 0.00 %

Figure 5. composition of outlet sample of biogas

IV. RESULTS AND DISCUSSION

i. The aim of this test was to reduced the amount of H_2S concentration present in biogas and conversion of the H_2S into elemental sulfur. verify and the behavior of gases other than H_2S and also to determine the catalyst deactivation time.
ii. The test demonstrated that the volume of solution used, containing 0.1 mol/l of ICS solution, is effective in removing present in the biogas.
iii. Results of this test, conducted using a volume of 1000 ml of catalyst solution, are presented in fig 6.

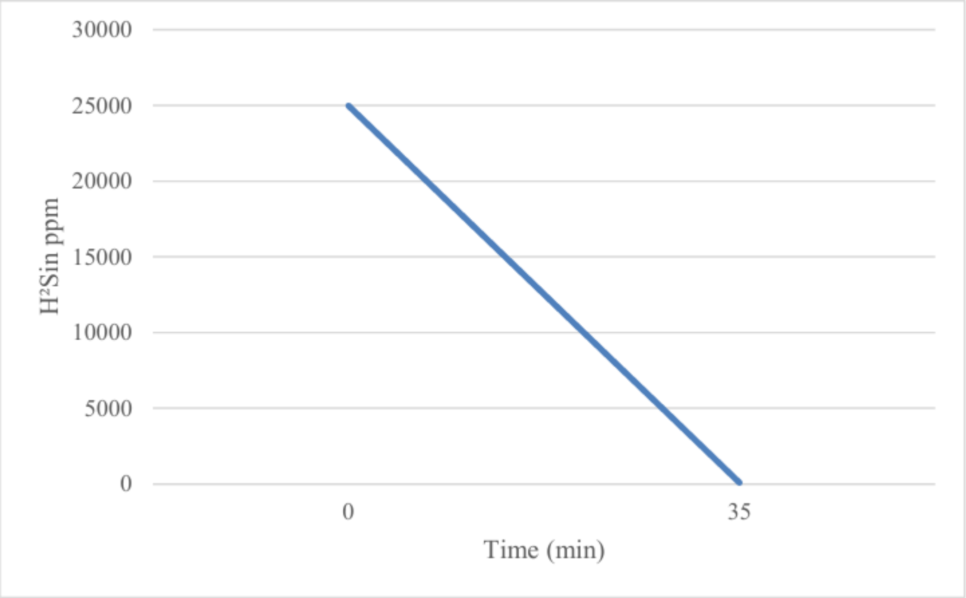


Figure 6. Showing H2S reduction

i. The catalytic solution begins to lose removal efficiency after 4 min and its complete deactivation occurs after 35 min., as illustrated in Fig 6.
ii. Biogas generated from spentwash contains CH_4 upto 55% to 70%, co_2 up to 30% to 45%, H_2S 2-3% (20000 -30000 ppm). Results in the Fig 7, demonstrate that compositions (without H_2S) of gases other than H_2S are maintained constant, except for the component CO_2, which is slightly absorbed at the beginning of bubbling, thus increasing the outlet composition of the CH_4.

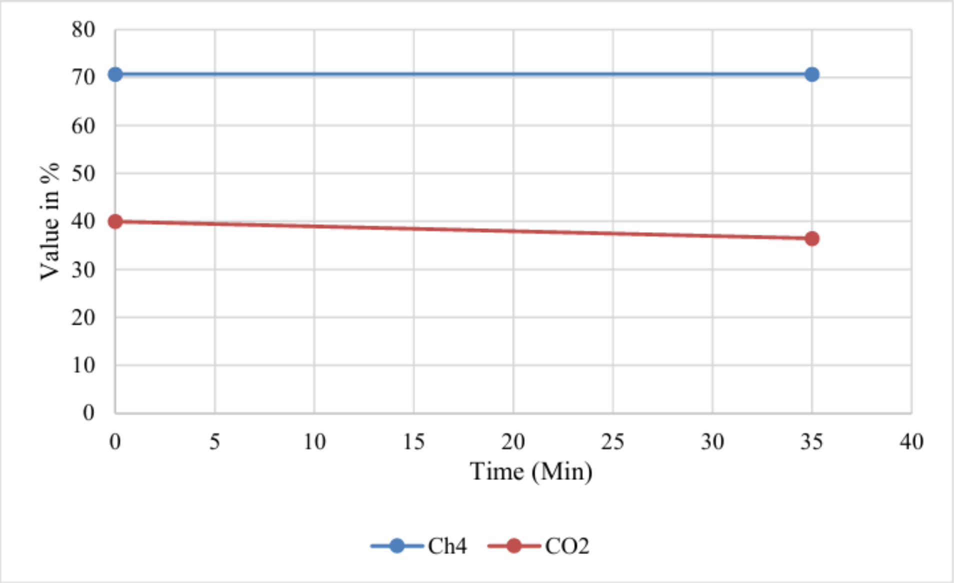


Figure 7. showingcCH4 and CO2 reduction

Table 1. Composition of raw biogas and treated biogas

Sr. No.	Composition	Raw Biogas	Treated Biogas	Unit
1	CH_4	70.75	70.75	%
2	CO_2	39.70	36.38	%
3	H_2S	25000	92	PPM

i. Above Table shows that the treated biogas contain 92 ppm ie 0.0092 % of H2S.
ii. The total amount of sulfur obtained from desulphurization of biogas was 25g.
iii. To confirm the identity of the yellow substance obtained from biogas desulphurization process a confirmatory taste was conducted. The result demonstrated that substance is indeed sulfur.

V. CONFIRMATORY TEST

i. Sulfur confirmation test (Lassaigne's Test)
ii. Take a small piece of dry sodium metal in a fusion tube and heat it gently till the metalmelts or fuses.
iii. Add equal quantity of compound to this fused metal (If the compound is a liquid then add two drops of it with a capillary) Heat it gently then strongly till it becomes red hot.
iv. Plung the red hot tube in 10 ml or ¾ of a test tube of distilled water taken in a porcelain dish, covering it immediately with an asbestos sheet crush the fusion tube completely.
v. Boil the extract for five minutes reduce the volume to about 5 ml and filter.
vi. Perform following test using this filtrate.

Table 2. Lassaigne's Test

Test	Observation	Inferences
1 ml of extract +1 ml of 2N Acetic Acid + 1 ml of Lead Ace tate Solution.	A black precipitate	Sulphur present.

i. Organic compound is fused with sodium metal, converting sulfur to sodium sulfide (Na_2S).
ii. The fused mass is dissolved in water, forming a solution containing Na_2S.
iii. Lead acetate ($Pb(CH_3COO)_2$) is added to the solution.
iv. If sulfur is present, the reaction between lead acetate and sodium sulfide produces lead sulfide (PbS), which is a black precipitate. This black precipitate is a clear visual indication of the presence of sulfur in the original organic compound.
$Na_2S(aq) + Pb(CH_3COO)_2(aq) \rightarrow PbS(s) + 2\,CH_3COONa(aq)$
v. The result demonstrated that substance is indeed sulfur.

VI. CONCLUSION

The findings from this study indicate that enhancing the quality of biogas by reducing HZS is achievable through an iron-chelated process that functions at ambient temperature. The results reveal that the nearly selective increase in the rate of H2S removal is just one of the benefits of this chemical absorption method. The primary advantage lies in the conversion of H2S into sulfur, effectively eliminating its pollution potential. The catalytic solution, Fe-EDTA, utilized in the experiments was formulated using disodium EDTA, a different salt than those typically referenced in existing literature. This specially prepared catalytic solution proved to be highly effective in removing H2S gas. After desulfurization, the biogas can be processed through a CO2 scrubber to yield pure methane, which can be directly utilized in industrial boilers or converted into BioCNG, offering a more economical alternative to fossil fuels. Additionally, the sale of recovered sulfur can create new revenue opportunities for biogas facilities, enhancing their financial sustainability. By replacing virgin sulfur with recovered sulfur, industries may lower their raw material expenses. It is essential to ensure the purity and quality of the recovered sulfur to facilitate its acceptance across various applications, which may necessitate advanced purification methods based on the specific intended use. Therefore, continued research and optimization of this approach could lead to more effective and sustainable gas treatment solutions in the future.

VII. REFERENCES

[1] P. Jaramillo, H.S. Matthews, Landfill-gas-to-energy projects: Analysis of net private and social benefits, Environ. Sci. Technol. 39 (2005) 7365e7373.
[2] S. Rasi, J. Lantel € € a, J. Rintala, Trace compounds affecting biogas energy utilisation-A review, Energy Convers. Manage 52 (2011) 3369e3375.
[3] G.M. Deshmukh, A. Shete, D.M. Pawar, Oxidative absorption of hydrogen sulfide using an iron-chelate based process: chelate degradation, J. Chem. Technol. Biotechnol. 88 (2013) 432e436.
[4] M. Miltner, A. Makaruk, J. Krischan, M. Harasek, Chemical-oxidative scrubbing for the removal of hydrogen sulphide from raw biogas: potentials and economics, Water Sci. Technol. 66 (2012) 1354e1360.
[5] C.F. Petre, S. Piche, A. Normandin, F. Larachi, Advances in chemical oxidation of total reduced sulfur from kraft mills atmospheric effluents, Int. J. Chem. React. Eng. 5 (2007) 88.
[6] J. Krischan, A. Makaruk, M. Harasek, Design and scale-up of an oxidative scrubbing process for the selective removal of hydrogen sulfide from biogas, J. Hazard Mater 215e216 (2012) 49e56.
[7] A.K. Dalai, M.T. Cundall, M. De, Direct oxidation of hydrogen sulphide to sulphur using impregnated activated carbon catalysts, Can. J. Chem. Eng. 86 (2008) 768e777.
[8] X. Zhang, Y. Tang, S. Qu, J. Da, Z. Hao, H2S-Selective catalytic oxidation: catalysts and processes, ACS Catal. 5 (2015) 1053e1067.
[9] K. Abolfazl, V. Leila, A.S. Ali, K. Mohammad, Experimental and theoretical studies of pressure swing adsorption process to remove H2S from methane in a packed bed, Sci. Res. Essays 5 (2010) 2391e2399.
[10] N. Heymans, S. Vaesen, G.D. Weireld, A complete procedure for acidic gas separation by adsorption on MIL-53 (Al), Microporous Mesoporous Mater 154 (2012) 93e99.
[11] M. Ozekmekci, G. Salkic, M.F. Fellah, Use of zeolites for the removal of H2S: a mini-review, Fuel Process Technol. 139 (2015) 49e60.
[12] A.M. Montebello, T. Bezerra, R. Rovira, L. Rago, J. Lafuente, X. Gamisans, et al., Operational aspects, pH transition and microbial shifts of a H2S desulfurizing biotrickling filter with random packing material, Chemosphere 93 (2013) 2675e2682.