CAPTURE OF HYDROGEN SULPHIDE FROM RAW BIOGAS AND PRODUCTION OF HIGH S-NUTRIENT NATURAL CHAR AND SLURRY FOR UTILIZATION IN SOIL HEALTH ENHANCEMENT

SHIVALI

CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY

INDIAN INSTITUTE OF TECHNOLOGY DELHI, INDIA

DECEMBER 2021

CAPTURE OF HYDROGEN SULPHIDE FROM RAW BIOGAS AND PRODUCTION OF HIGH S-NUTRIENT NATURAL CHAR AND SLURRY FOR UTILIZATION IN SOIL HEALTH ENHANCEMENT

by

SHIVALI

CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY

Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy
to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI
DECEMBER 2021

CERTIFICATE

It is certified that the thesis entitled "**CAPTURE OF HYDROGEN SULPHIDE FROM RAW BIOGAS AND PRODUCTION OF HIGH S-NUTRIENT NATURAL CHAR AND SLURRY FOR UTILIZATION IN SOIL HEALTH ENHANCEMENT**," being submitted by **Ms. Shivali** to the Indian Institute of Technology Delhi, is a record of the student work carried out by her. She has worked under our supervision and guidance, and has fulfilled the requirements for the submission of this thesis, which has attained the standard required for a Ph. D. degree of the Institute.

The results presented in this thesis have not been submitted elsewhere for the award of any degree or diploma.

Dated: 31st August, 2021

Vijay

(Prof. Virendra Kumar Vijay)
Professor
Centre for Rural Development & Technology
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi – 110016, INDIA

P. M. V. Subba Rao

(Prof. P. M. V. Subbarao)
Professor
Department of Mechanical Engineering
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi – 110016, INDIA

Chandra

(Prof. Ram Chandra)
Assistant Professor
Centre for Rural Development & Technology
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi – 110016, INDIA

ACKNOWLEDGEMENTS

First and foremost, I wish to express my deepest gratitude and indebtedness to my ***supervisors*** **Prof. P. M. V. Subbarao, Prof. V.K. Vijay** and **Prof. Ram Chandra** for their continuous guidance, encouragement, consistent, inspiring guidance and utmost cooperation at every stage throughout the study. I must thank them for sharing their immense knowledge and for inculcating the basics of research in me. It was a highly educative and memorable experience working under their supervision which has provided a deep insight to the world of research. The determination, dedication and discipline of Prof. P.M.V.Subbarao have been the inspiration for me to complete this work. The consistent encouragement, continuous monitoring and commitments to the excellence of Prof. V.K. Vijay have always motivated me to improve my work and use the best of my capabilities I express my deep gratitude to Prof. Ram Chandra who advised me to overcome hurdles, helped me through difficulties and encouraged me in the slowdown. **All of them provided me with a long-lasting bearing on my understanding of life and thought processes.**

I express my deepest gratitude to the esteemed members of my Student Research Committee, **Prof. K.K. Pant** (External Examiner), Professor and Head, Department of Chemical Engineering, **Prof. S. N. Naik**, (Chairperson), and **Prof. Hariprasad P.** (Internal Examiner) for their valuable comments, reviews and supports.

I am grateful to the Indian Institute of Technology, Delhi for providing me with the research facilities and financial support. My heartfelt thanks to all my colleagues and friends of my laboratory, i.e., **Ms. Goldy Shah, Mr. Himanshu Kumar, Mr. Sameer Ahmad Khan, Mr. Subodh Kumar, Ms. Adya Isha, Ms. Swapna Sagarika Sahoo, Mr. I. K. Biju** and all biogas

research lab group for their valuable support for creating a conducive work environment and helping me in the time of need. I would like to thank all my seniors **Dr. Pooja Ghosh, Dr. Rimika Kapoor Dr. Vandit Vijay, Dr. Pushpendra Kumar** and **Dr. L.D. Kala** for their guidance and informal support in pursuing this research work and providing me the mentorship opportunity in their research. I would like to use this opportunity to thank **Mr. Mahesh Verma** and **Mr. Vinod Kumar** who have constantly helped me on all technical issues during the course of experimental studies at various stages of work. I wish to take this opportunity to extend my thanks to my hostel mates, **Dr. Seema Kewat, Mrs. Vasudha Aggarwal** and **Dr. Abhilasha Pawar**, who supported and inspired me during my stay in '*Himadri'* house.

I would also like to thank **Prof. P.M.V. Subbarao (**Head, CRDT), and other faculty members of CRDT, IIT Delhi with whom I interacted occasionally. My heartfelt thanks are due to all the staff members of the Centre, especially **Ms. Seema Bharti** for her help during the research work. I am likewise thankful to those who have directly or indirectly helped me to finish my dissertation study.

I would like to extend my deepest gratitude to my parents, and in-laws for their constant support and encouragement throughout the course of study. My deepest love, appreciation and indebtedness go to ***my father*** **- Mr. Desh Raj Sahota** for his dreams, sacrifices and wholeheartedly endorses. His trust in my capabilities has always motivated me to reach higher academic degrees. I would like to convey my unbounded love to ***my mother*** **- Mrs. Prem Lata Sahota** as I spent a major part of my childhood in her lap. A great deal of effort, endurance, encouragement and blessings from my parents. Moreover I wholeheartedly thank ***my loving brother*** **- Mr. Shubham**, and ***my husband*** **Mr. Dhruv Singh** for their unconditional love and cooperation, without which this study would not have been possible. I express my sincere gratitude to my husband for listening to my never-ending woes and encouraging me during the toughest phases of my work.

My sincere thanks to my In-Laws **Mr. Shripal Singh and Mrs. Geeta Devi** for their love, countless blessings, affection, incessant inspiration and support because of which I have made it through all the steps to reach this point in life.

I take this opportunity to thank the great assets of my life, my friend **Ms. Goldy Shah** and my senior **Dr. Vaibhav Koutu**, to share my joy, my sorrow and happiness *who helped me to accomplish this arduous work.*

At last but not the least, I am beholden to almighty for their blessings to help me to raise my academic level to this stage. I pray for their benediction in my future endeavours. Their blessings may be showered on me for strength, wisdom and determination to achieve in future.

New Delhi
Date: 2nd September, 2021 **Shivali**

ABSTRACT

The present work focuses on the removal of hydrogen sulphide (H_2S) from biogas via sustainable approach. So, this study aims to develop an adsorption based hydrogen sulphide removal reactor using char and spent slurry of biodigester. De-oiled cakes of pongamia is used for production of biogas in a 20 cubic meter digester. The study is divided into two levels namely, initial feasibility study and performance study of a model packed bed reactor. As the primary targeted users in this study are rural entrepreneurs, the char was produced using waste leaves, Mixed Leaf waste was carbonised at three different temperatures 200 °C, 300 °C and 400 °C through slow pyrolysis for a period of 3 hours using a traditional kiln. Consequently, biochar prepared from mixed leaf waste at different temperatures 200 °C, 300 °C and 400 °C, are denoted as LWB200, LWB300, and LWB400, respectively. The biochar generated in the kiln was ground to a mesh size less than 500 microns. A detailed characterization of prepared biochar as well as H_2S adsorbed biochar (after saturation) was done. Moreover, freshly prepared biochar and saturated biochar were characterized using series of characterizations including CHNS elemental analysis, Brunauer–Emmett–Teller (BET) analysis, Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy and Energy Dispersive Spectrometer (SEM-EDX) to develop an insight into the adsorption mechanism.

After detailed characterization, LWB400 was found to be a promising adsorbent for desulphurization of biogas with high H_2S removal efficiency during feasibility study. Thus, LWB400 leaf waste biochar was used for further detailed performance study. An evaluation of the adsorption capacity of leaf waste biochar in terms of mg H_2S removal per gram of biochar was also determined. Also, a suitable equilibrium isotherm model was identified to describe

the current adsorption process. The detailed optimization of parameters like the effect of flow rate and the effect of pressure was done. The adsorption isotherm equilibrium models were examined for comprehending the adsorption process of H_2S better and their associated parameters were determined. This optimization would help to determine the best suitable pressure and flow rate required for efficient H_2S removal. It was concluded that the highest adsorption capacity is 15.9 mg H_2S/g with removal efficiency of 98.6 % was obtained at flow rate of 3 m^3/h and pressure of 3 bar. However, at flow rate, 3 m^3/h and pressure 2 bar with the adsorption capacity of 15.1 mg H_2S/g and removal efficiency 98.4 %, which was found to be the best possible condition for biogas desulphurization in terms of breakthrough time and lesser energy consumption. The isotherm analysis results showed that the Freundlich isotherm model with a higher R^2 value of H_2S is 0.9903, which is the most suitable to describe the adsorption isotherm of H_2S. So, it was concluded from the current adsorption isotherm data that the adsorption process is multilayer, not monolayer. These obtained results provides an insight into the H_2S adsorption mechanism onto the biochar. This was attributed to higher pH which led to an increased rate of dissociation of H_2S and higher elemental sulphur conversion rates. Amongst several factors affecting H_2S adsorption, the surface area played an important role in adsorption along with the associated factors like higher alkaline pH, carbonization temperature and mineral elements present on the surface of biochar. The SO_4^{2-} produced in the biochar was more likely to combine with Ca and K (mineral elements) to form useful sulphates for soil health enhancement. Finally, the reusability and practical applications of the saturated biochar as a soil ameliorant were investigated to reduce environmental impact and solve problems associated with the saturated adsorbent disposal. S-enriched biochar is proven as a beneficial agricultural S fertilizer for promoting mustard crops or other oil-producing crops, which can become bioavailable to plants as S-micronutrient. Therefore, the plot experiments of saturated biochar were done to utilize S-enriched biochar for crop production of *Brassica nigra* (Mustard seeds). From the results, it was observed that the amending S-enriched biochar resulted in significant enhancement of the physiological indexes including plant height, fresh and dry weight, and accumulation of nutrients like N, P, K, S, Na, Mg, and Fe in mustard crop with 4 times increase in S content as compared to plot with no amendment (Blank).So it was concluded that the present approach of H_2S removal results in the sustainable production of organic nutrient with efficient H_2S removal via a holistic approach.

On the other hand, an alternative technology for utilizing biogas digested slurry for biogas desulphurization is discussed as well as nutrient value enrichment in saturated slurry. It was observed that the highest removal efficiency of 88.7% obtained at pressure 1 bar and flow rate 2 m^3/h with outlet H_2S concentration 115 ppm. The total experiment run was of 41 hours for 25 L (5% TS) of biogas slurry with a total of 73.5 m^3 biogas was treated. After saturation, the spent slurry was assessed for nutrient value addition. From the results, it was witnessed that after treatment digested slurry gets enriched about two times with sulphur S (%) than initial sulphur S (%) present in the untreated slurry. Also the P (%) and N (%) showed a visible increase after H_2S treatment.

सार

वर्तमान कार्य टिकाऊ दृष्टिकोण के माध्यम से बायोगैस से हाइड्रोजन सल्फाइड (H_2S) को हटाने पर केंद्रित है। इसलिए, इस अध्ययन का उद्देश्य बायोचार और बायोडाइजेस्टर के खर्च किए गए घोल का उपयोग करके एक सोखना आधारित H_2S हटाने रिएक्टर विकसित करना है। पोंगामिया के तेल रहित केक का उपयोग 20 घन मीटर डाइजेस्टर में बायोगैस के उत्पादन के लिए किया जाता है। अध्ययन को दो स्तरों में विभाजित किया गया है, प्रारंभिक व्यवहार्यता अध्ययन और एक मॉडल पैक बेड रिएक्टर का प्रदर्शन अध्ययन।चूंकि इस अध्ययन में प्राथमिक लक्षित उपयोगकर्ता ग्रामीण उद्यमी हैं, बायोचार का उत्पादन बेकार पत्तों का उपयोग करके किया गया था, मिश्रित पत्ती के कचरे को तीन अलग-अलग तापमान 200°C, 300°C और 400°C पर धीमी पायरोलिसिस के माध्यम से 3 घंटे की अवधि के लिए पारंपरिक भट्टी का उपयोग करके कार्बोनाइज किया गया था। भट्टे में उत्पन्न बायोचार को 500 microns से कम की जाली के आकार में पीस दिया गया था। नतीजतन, अलग-अलग तापमान 200°C, 300°C और 400°C पर मिश्रित पत्ती के कचरे से तैयार बायोचार को क्रमशः LWB200, LWB300 और LWB400 के रूप में दर्शाया जाता है। बायोचार तैयार करने के बाद, तैयार बायोचार के साथ-साथ H_2S सोखने वाले बायोचार (संतृप्ति के बाद) का विस्तृत लक्षण वर्णन किया गया। इसके अलावा, ताजा तैयार बायोचार और संतृप्त बायोचार को सीएचएनएस(CHNS) तात्विक विश्लेषण, ब्रूनौर-एम्मेट-टेलर ((BET)) विश्लेषण, एटेन्यूएटेड टोटल रिफ्लेक्शन फूरियर ट्रांसफॉर्म इन्फ्रारेड स्पेक्ट्रोस्कोपी (ATR-FTIR), एक्स-रे डिफ्रैक्शन (XRD) सहित कई विशेषताओं का उपयोग करके विशेषता दी गई थी।सोखना तंत्र में अंतर्दृष्टि विकसित करने के लिए स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी और एनर्जी डिस्पर्सिव स्पेक्ट्रोमीटर (SEM-EDX)।

विस्तृत लक्षण वर्णन के बाद, LWB400 को बायोगैस के डिसल्फराइजेशन के लिए एक आशाजनक सोखना के रूप में पाया गया, जो LWB200, LWB300 और LWB400 के बीच अत्यधिक कुशल बायोचार है। इस प्रकार, पैक्ड बेड रिएक्टर में कुशल H_2S निष्कासन प्रयोगों के लिए लीफ वेस्ट बायोचार (LWB400) का उपयोग विस्तृत अध्ययन के लिए किया जाता है। इस अध्ययन में पैक्ड बेड रिएक्टर में कच्चे बायोगैस में मौजूद H_2S को हटाते समय लीफ वेस्ट बायोचार की सोखने की क्षमता का मूल्यांकन किया गया। इसके अलावा, वर्तमान सोखना प्रक्रिया का वर्णन करने के लिए एक उपयुक्त संतुलन इसोथर्म मॉडल की पहचान की जाती

है। प्रवाह दर के प्रभाव और दबाव के प्रभाव जैसे मापदंडों का विस्तृत अनुकूलन किया गया था। सोखना समतापी संतुलन मॉडल की जांच की गई ताकि H_2S की सोखना प्रक्रिया को बेहतर ढंग से समझा जा सके और उनके संबंधित मापदंडों का निर्धारण किया गया। यह अनुकूलन कुशल H_2S हटाने के लिए आवश्यक सर्वोत्तम उपयुक्त दबाव और प्रवाह दर निर्धारित करने में मदद करेगा । यह निष्कर्ष निकाला गया कि 98.6% की निष्कासन दक्षता के साथ उच्चतम सोखना क्षमता 15.9 mg H_2S/g है, जो 3 m^3/h की प्रवाह दर और 3 बार के दबाव पर प्राप्त की गई थी।

हालांकि, प्रवाह दर पर 3 m^3/h और दबाव 2 bar 15.1 mg H_2S/g की सोखना क्षमता और 98.4% हटाने की क्षमता के साथ, जो कि सफलता के समय के मामले में बायोगैस डिसल्फराइजेशन के लिए सर्वोत्तम संभव स्थिति और कम ऊर्जा की खपत पाई गई थी । इसोथर्म विश्लेषण के परिणामों से पता चला है कि H_2S के उच्च R^2 मान के साथ फ्रायंडलिच इज़ोटेर्म मॉडल 0.9903 है, जो H_2S के सोखना इसोथर्म का वर्णन करने के लिए सबसे उपयुक्त है। इसलिए, वर्तमान सोखना इसोथर्म डेटा से यह निष्कर्ष निकाला गया कि सोखना प्रक्रिया बहुपरत है, न कि मोनोलेयर। ये प्राप्त परिणाम बायोचार पर H_2S सोखना तंत्र में एक अंतर्दृष्टि प्रदान करते हैं। यह उच्च pH के लिए जिम्मेदार ठहराया गया था जिसके कारण H_2S के पृथक्करण की दर में उच्च मौलिक और सल्फर रूपांतरण दरवृद्धि हुई । H_2S सोखना को प्रभावित करने वाले कई कारकों में, सतह क्षेत्र ने उच्च क्षारीय pH, कार्बोनाइजेशन तापमान और बायोचार की सतह पर मौजूद खनिज तत्वों जैसे संबद्ध कारकों के साथ सोखने में महत्वपूर्ण भूमिका निभाई। बायोचार में उत्पादित SO_4^{2-} के Ca और K (खनिज तत्व) के साथ मिलकर मिट्टी के स्वास्थ्य को बढ़ाने के लिए उपयोगी सल्फेट बनाने की अधिक संभावना है। अंत में, मृदा सुधारक के रूप में संतृप्त बायोचार के पुन: प्रयोज्य और व्यावहारिक अनुप्रयोगों की जांच पर्यावरणीय प्रभाव को कम करने और संतृप्त सोखना निपटान से जुड़ी समस्याओं को हल करने के लिए की गई थी। S-समृद्ध बायोचार सरसों की फसलों या अन्य तेल उत्पादक फसलों को बढ़ावा देने के लिए एक लाभकारी कृषि S-उर्वरक के रूप में सिद्ध होता है, जो पौधों के लिए S-सूक्ष्म पोषक तत्व के रूप में जैवउपलब्ध हो सकता है। इसलिए, *Brassica nigra* (सरसों के बीज) के फसल उत्पादन के लिए एस-समृद्ध बायोचार का उपयोग करने के लिए संतृप्त बायोचार के प्लॉट प्रयोग किए गए थे। परिणामों से, यह देखा गया कि संशोधन (रिक्त) वाले भूखंड मुक़ाबिले में S-समृद्ध बायोचार के परिणामस्वरूप पौधों की ऊंचाई, ताजा और सूखे वजन, N, P, K, S, Na, Mg, Fe जैसे पोषक तत्वों के संचय सहित शारीरिक सूचकांक में

S सामग्री में 4 गुना महत्वपूर्ण वृद्धि हुई। इसलिए यह निष्कर्ष निकाला गया कि H_2S हटाने के वर्तमान दृष्टिकोण के परिणामस्वरूप समग्र दृष्टिकोण के माध्यम से कुशल H_2S हटाने के साथ जैविक पोषक तत्व का स्थायी उत्पादन होता है।

दूसरी ओर, बायोगैस डीसल्फराइजेशन के लिए बायोगैस डाइजेस्ट स्लरी के उपयोग के लिए एक वैकल्पिक तकनीक के साथ-साथ संतृप्त घोल में पोषक तत्व मूल्य संवर्धन पर भी चर्चा की गई है। यह देखा गया कि आउटलेट H_2S एकाग्रता 115 ppm के साथ दबाव 1 bar और प्रवाह 2 m^3/h पर 88.7% की उच्चतम निष्कासन दक्षता प्राप्त हुई। कुल 73.5 m^3 बायोगैस के साथ बायोगैस घोल के 25 लीटर (5% TS) के लिए कुल प्रयोग 41 घंटे का था। संतृप्ति के बाद, पोषक तत्व मूल्यवर्धन के लिए खर्च किए गए घोल का मूल्यांकन किया गया था। परिणामों से, यह देखा गया कि उपचार के बाद पचा हुआ घोल अनुपचारित घोल में मौजूद प्रारंभिक सल्फर S (%) की तुलना में उपचार के बाद सल्फर S (%) लगभग दो गुना समृद्ध हो जाता है। साथ ही P (%) और N (%) ने H_2S उपचार के बाद एक स्पष्ट वृद्धि दिखाई।

TABLE OF CONTENTS

CHAPTER VII Conclusions and Scope of Future Studies 120-126

LIST OF FIGURES

LIST OF TABLES

SYMBOLS AND ABBREVIATIONS

% = Percent

& = And

/ = Per

< = Lower than

> = Greater than

0 = Degree

ρ = Density

η = Efficiency

μ = Viscosity

^0C = Degree celsius

C = Carbon

H = Hydrogen

C/N = Carbon to nitrogen ratio

H_2S = Hydrogen sulphide

CH_4 = Methane

cm = Centimetre

kg = Kilo gram

CNG = Compressed natural gas

SO_2 = Sulphur dioxide

CO_2 = Carbon dioxide

Conc. = Concentration

C_{in} = Inlet concentration

C_{out} = Outlet concentration

C_o = Initial concentration

RE = Removal efficiency

EC = Elimination capacity

EBRT = Empty bed residence time

MW_{H2S} = Molecular weight of H_2S

m_{ads} = Mass of adsorbent used

Q = Adsorption capacity

q = Flow rate

T_B = Breakthrough time

V_M = Molar volume

C = Breakthrough concentration

LWB = Leaf waste based biochar

$\mathrm{LWB_S}$ = Sulphur enriched leaf waste based biochar

BDS = Biogas digested slurry

STP = Standard temperature pressure