DEVELOPMENT OF SUSTAINABLE BIOMATERIALS FOR BIOMETHANE AND CARBON DIOXIDE ADSORPTION

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by

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Dedicated to my

grandparents, parents,

and

Late Dr. Ram Chandra

CERTIFICATE

This is to certify that the thesis entitled "Development of Sustainable Biomaterials for Biomethane and Carbon dioxide Adsorption", being submitted by Mr. Komalkant Adlak to the Indian Institute of Technology Delhi for the award of "Doctor of Philosophy" is a record of bonafide research work carried out by him. He has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

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Komalkant Adlak

Abstract

The unprecedented challenge of climate change outlines the failure on environmental parameters despite remarkable developments in the previous two and a half centuries. Fossil fuels have been a convenient energy source for long periods; however, their consumption has majorly contributed to mounting levels of carbon emissions. Now, developing alternative energy sources is imperative and anaerobic digestion technology has a crucial role in the transition. Renewable methane is obtained from organic waste digestion and biogas separation thereafter. The key challenge is storing the methane-rich gas where it is currently stored by compressing it at a very high pressure of 20-25 MPa. Alternatively, in adsorption based storage where similar amount of gas (as of compression) is stored under mild pressure. The storage is obtained in a porous material-filled cylinder, where gas is adsorbed under pressure on the microporous surface. The density of gas storage is higher in microporous materials than in simple compression, which reduces the storage pressure requirement. The porous materials obtained from biomass have been another advantage of this technology since they are renewable, and utilising such a source also reduces the environmental burden. The biomass is first carbonised to obtain char and then converted to high surface area activated carbons using activation. In this thesis work, the focus have been on such biomass-based sustainable materials and tailored their production for high-efficiency gas storage and capture.

In the first Objective, biochar's combined physical and chemical activation was explored. Potassium hydroxide has been used for chemical activation and steam as physical activation source to reduce chemical use to obtain high surface area. The combined activated carbons have a surface area of 963 m^2g^{-1} compared to only chemically activated 764 m^2g^{-1}. For the analysis of biomethane adsorption, the pellets were prepared using bentonite and Kaolin. The best results obtained were found with 20% (weight basis) of Kaolin with gravimetric methane uptake of 0.28 g/g and volumetric methane uptake of 231 v/v with 177 v/v of deliverable capacity.

In second work, the various nature biomass has been selected and pore formation pattern has been studied. The activated carbons were synthesized from ten different biomasses under similar activation conditions. The selection has taken place based on the nature (hardness/softness) and their local availability. These prepared carbons were then analysed with different techniques such as BET, X-ray diffraction, Scanning electron

microscope, and FT-infrared. The biomass's nature has an influence on the pores' distribution on the material and hence different methane adsorption capacities. The highest volumetric ratio of ~251 v/v (uptake), ~217 v/v (delivery) has been recorded on coconut shell AC, whereas the highest gravimetric uptake of ~0.32 g/g at 6.5 MPa was recorded on karanja shell AC.

Next, the efforts were made to address the challenge of lower desorption of the gas while system operation since thermodynamics discourages overall technological development. The adsorption was carried out at room temperature and desorption by placing gas-filled cylinders in a water bath at different temperatures maintained at 40, 45, 50 and 55 °C. At room temperature, nearly 54% of adsorbed gas is released whereas, at 55 °C, approximately 80% of the gas is recovered.

Adsorption-based technology was also assessed using Life cycle Assessment as a tool including its comparison with compression-based storage system. The activated carbon-based storage system has been efficient on the environmental parameters however few points to be considered. Lower pressure storage reduces cylinder thickness increases safety as well it also reflects on the midpoint indicators as well. However, the chemical synthesis of activated carbons is still a key concern, and recycling waste during production is crucial in reducing environmental burdens.

Lastly, the activated carbon was prepared with focusing on its heteroatom content and improving sustainability. In this work, the materials have been explored for their application in carbon dioxide capture e.g. from biogas and post-combustion gases. The material synthesised has a considerable presence of nitrogen and sulphur with high oxygen content. They are prepared via the hydrochar route and activated using $KCl+Na_2S_2O_3$ to activate hydrochar, resulting in high surface area and porosity. The prepared activated carbons achieved high CO_2 uptake of up to 3.5 mmol/g. The influence of heteroatom on CO_2 was also investigated in the study. These materials also shows high regenerable capacity over five cycles.

Further, large-scale development of these materials for successful gas capture and storage technologies application would be vital for sustainable development. The widespread technological application would develop and strengthen new avenues towards rural industrialisation.

सारांश

जलवायु परिवर्तन की अभूतपूर्व चुनौती हमें बताती है कि पिछले दो और आधे सदी में चमत्कारी विकासों के बावजूद, पर्यावरणीय मापदंडों पर नाकामी ही हासिल की है। जीवाश्म ईंधन इतनी समय तक ऊर्जा का सुखद स्रोत रहे हैं, हालांकि, उनका उपभोग प्रमुख रूप से कार्बन उत्सर्जन के स्तरों में योगदान किया है। अब, विकल्पिक ऊर्जा स्रोतों का विकास आवश्यक है, और एनोरोबिक डाइजेशन जैसी प्रौद्योगिकी की इस ऊर्जा परिवर्तन में महत्वपूर्ण भूमिका है। नवीकरणीय मीथेन जैविक अपशिष्ट पाचन और प्राप्त बायोगैस विभाजन से हासिल किया जाता है। मुख्य चुनौती मीथेन युक्त गैस का भंडारण करना है, वर्तमान में बहुत उच्च 20-25 MPa तक दबाकर कहाँ संग्रहित किया जाता है। वैकल्पिक रूप से, अधिशोषण आधारित भंडारण में जहां समान मात्रा में गैस (संपीड़न के रूप में) हल्के दबाव में संग्रहीत की जा सकती है। गैस का भंडारण छिद्रपूर्ण सामग्री से भरे सिलेंडर में प्राप्त किया जाता है, जहां गैस को सूक्ष्म छिद्रित सतह पर दबाव में सोख लिया जाता है। गैस संग्रहण माइक्रोपोरस सामग्रियों में साधारित कमजोर दब की तुलना में अधिक है, जिससे अंत में भंडारण दबाव की आवश्यकता कम हो जाती है। बायोमास से प्राप्त किए गए माइक्रोपोरस सामग्रियों का लाभ यह है कि वे पुनर्नवीनी हैं और इस तरह की स्रोत का उपयोग करने से पर्यावरणीय बोझ भी कम होता है। बायोमास को कार्बनीकरण प्रक्रिया द्वारा पहले बायोचार में परिवर्तित किया जाता है, और फिर उसे रसायनो का उपयोग करके उच्च सतह क्षेत्र सक्रिय कार्बन्स में रूपांतरित किया जाता है। इस थीसिस में, इस प्रकार के बायोमास आधारित सामग्रियों, और उनके उच्च क्षमता गैस संग्रह और कैद के लिए उनके उत्पादन पर ध्यान केंद्रित किया है।

पहले उद्देश्य में, बायोचार को संयुक्त भौतिक और रासायनिक प्रक्रिया के संयोजन का अन्वेषण किया है। पोटैशियम हाइड्रॉक्साइड रासायनिक सक्रियकरण और भाप भौतिक सक्रियकरण के तरह उपयोग किया गया है। संयुक्त सक्रियकरण कार्बन्स का सतह क्षेत्र 963 मीटर वर्ग/ग्राम जो की, तुलनात्मक रूप से केवल रासायनिक रूप से प्राप्त पदार्थ, 764 मीटर वर्ग/ग्राम से अधिक है। बायोमीथेन अधिशोषण का विश्लेषण के लिए, बेंटोनाइट और कैओलिन का उपयोग करके पेलेट्स भी तैयार की हैं। प्राप्त किए गए सर्वश्रेष्ठ परिणाम में 20% (वजन के आधार पर) कैओलिन के साथ 0.28 ग्राम/ग्राम भार की मीथेन, अधिशोषण क्षमता 231 v/v और प्रदेय क्षमता के 177 v/v के साथ मिला है।

दूसरे कार्य में, विभिन्न प्रकृति के बायोमास का चयन किया और उनके सतही छिद्र निर्माण प्रतिरूप का अध्ययन किया गया है। यहाँ समान सक्रियकरण की शर्तों के तहत दस विभिन्न जैविक स्रोतों से सक्रिय कार्बन उत्पन्न किया है। चयन उनकी भौतिक प्रकृति और उनकी स्थानीय उपलब्धता पर निर्भर है। ये तैयार किए गए कार्बन्स को फिर विभिन्न तकनीकों जैसे कि BET, एक्स-रे डिफ्रेक्शन, स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोप, और एफटी-इन्फ्रारेड के साथ विश्लेषण किया गया है। बायोमास की प्रकृति उनके छिद्र निर्माण को प्रभावित करती है, और इसलिए विभिन्न मीथेन संचयन में भिन्नता प्राप्त होती है। नारियल शैल सक्रिय कार्बन पर लगभग 251 v/v (अधिशोषण), 217 v/v (प्रदेय) का सर्वोच्च आयतन अंश, जबकि करंजा शैल सक्रिय कार्बन पर 6.5 MPa में लगभग 0.32 g/g का सर्वोच्च गैस अधिग्रहण दर्ज हुआ है।

अगले कार्य में, प्रणाली क्रियान्वयन के दौरान गैस के कम निकालने की चुनौती को संबोधित करने का प्रयास किया है। प्रौद्योगिकी की ऊष्मप्रवैगिकी नियम गैस मुक्ती को हतोत्साहित करता है। कमरे के तापमान पर गैस का अधिशोषण करके विभिन्न तापमानों 40, 45, 50 और 55 °C पर पानी के वातवरण में गैस मुक्ती प्रक्रिया का अध्ययन किया। कमरे की तापमान पर, करीब 54% गैस मुक्त हो रही है, जबकि, 55 °C पर करीब 80% गैस पुनर्प्राप्त हो रही है।

जीवन चक्र मूल्यांकन के द्वारा इस अधिशोषण आधारित प्रौद्योगिकी का निरूपण और संपीड़न आधारित भंडारण के साथ तुलनात्मक अध्ययन भी किया है। सक्रिय कार्बन आधारित भंडारण प्रणाली पर्यावरण संबंधित पैरामीटर्स पर यह प्रभावी है, हालांकि कुछ बिंदुओं का विचार किया जाना चाहिए। कम दबाव भंडारण सिलेंडर की मोटाई को कम करता है, सुरक्षा को बढ़ाता है, यह मध्यबिंदु सूचकों पर प्रतिबिम्बित भी होता है। हालांकि, सक्रिय कार्बन के रासायनिक उत्पादन अभी भी मुख्य चिंता है और उत्पादन के दौरान कचरे का पुनःप्रयोग करना पर्यावरण पर बोझ को कम करता है।

अंत में, विषम परमाणु संपन्न पदार्थ पर ध्यान केंद्रित करके सक्रिय कार्बन तैयार किया है और उनके दीर्घकालिक उत्पादन में सुधार किया। इस कार्य में, इन सक्रिय कार्बन का उपयोग बायोगैस और दहन गैसों गैस से प्राप्त कार्बन डाइऑक्साइड कैप्चर में किया गया है। इन सक्रिय कार्बन में पर्याप्त नाइट्रोजन और सल्फर मौजूद है, जबकि ऑक्सीजन की उपस्थति प्रचूर मात्रा में हैं। इन्हें हाइड्रोचार मार्ग से तैयार किया जाता है, और हाइड्रोचार को सक्रिय करने के लिए $KCl+Na_2S_2O_3$ का उपयोग किया जाता है, जिससे उच्च सतही क्षेत्र और सरंध्रता प्राप्त होती है। तैयार सक्रिय कार्बन पर 3.5

mmol/g तक का उच्च CO_2 अवशोषण प्राप्त किया गया। अध्ययन में CO_2 पर विषम परमाणु के प्रभाव की भी जांच की गई। ये सामग्रियां पांच चक्रों में उच्च पुनर्योजी क्षमता भी दर्शाती हैं।

इसके अतिरिक्त, इन सामग्रियों के बड़े पैमाने पर विकास के सफल अनुप्रयोग, गैस कैप्चर और स्टोरेज प्रौद्योगिकियों के विकास के लिए महत्वपूर्ण होगा। व्यापक तकनीकी अनुप्रयोग नए ग्रामीण औद्योगिकी की दिशाओं को विकसित और मजबूत करेगा।

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Abbreviations

GHG	Green House gases
CO_2	Carbon dioxide
CH_4	Methane
N_2	Nitrogen
O_2	Oxygen
MJ	Mega Joule
Kg	Kilo Gram
km	Kilo meter
bio-CO_2	Biogenic CO_2
MEA	Monomethylamine
MOF	Metal-organic frameworks
CMS	Carbon molecular sieves
AC	Activated carbons
CCS	Carbon capture and storage
BECCS	Bioenergy with carbon capture and storage
L	Litre
STP	Standard temperature and pressure
NTP	Normal temperature and pressure
MPa	Mega Pascal
CNG	Compressed natural gas
LNG	Liquified natural gas
ANG	Adsorbed natural gas
K	Kelvin
v/v	volume/volume (cm^3 or L)
g/g	gram/gram
DoE	Department of Energy
atm	Atmospheric pressure
IUPAC	International union of pure and applied chemistry
SDG	Sustainable development goals
NNBOMP	New National Biogas and Organic Manure Programme
GOBAR	Galvanizing Organic Bio-Agro Resources
SATAT	Sustainable Alternative Towards Affordable Transportation
CBG	Compressed Biogas
LPG	Liquified petroleum gas
PSA	Pressure swing adsorption
BET	Brunauer–Emmett–Teller
SEM	Scanning electron microscope
FTIR	Fourier transform Infrared
XRD	X-ray diffraction
LCA	Life Cycle Assessment
MS	Molecular sieves
PAFs	Porous aromatic frameworks
NLDFT	Non-local density function theory
ISO	International standard organisation
MPSD	Micropore size distribution
MOVE	Methane opportunities for vehicular energy
wt	Weight

Å	Angstrom
KOH	Potassium Hydroxide
KCl	Potassium Chloride
HCl	Hydrogen chloride
$K_2C_2O_2$	Potassium oxalate
K_2CO_3	Potassium Chloride
NaOH	Sodium hydroxide
$NaNH_2$	Sodium amide
H_3PO_4	Phosphoric acid
$ZnCl_2$	Zinc Chloride
ACC	Chemically activated carbons
ACPC	Physicochemically activated carbons
GAC	Granular activated carbons
RoW	Rest of the world
CML	Centrum voor Milieukunde Leiden
IPCC	Intergovernmental panel on climate change
CAC	Chemically activated carbon
PAC	Physically activated carbon
CACR	Chemically activated carbon with waste recovery
HTC	Hydrothermal carbonization
TS	Total solid
DC	De-oiled cake (Kanranja)
SW	Softwood
C	Cellulose
TGA	Thermogravimetric analyser
HDC	De-oiled cake hydrochar
ACDC	De-oiled cake activated carbon
K_2CO_3	Potassium carbonate
K_2O	Potassium oxide
B	Bentonite
K	Kaolin
S	Sugar
nm	Nanometer
MPD	Mean pore diameter
CCSAC	Coconut shell activated carbons
h	hour