CO₂ Adsorption From The Methane-Rich Stream Using Bio-Adsorbent

by

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A Thesis
presented to
The University of Guelph

In partial fulfilment of requirements
for the degree of
Master of Applied Science
in
Engineering

Guelph, Ontario, Canada
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ABSTRACT

CO₂ ADSORPTION FROM THE METHANE-RICH STREAM USING BIO-ADSORBENT

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In this study, switchgrass was used as the feedstock to develop bio-adsorbent via hydrothermal pre-treatment with and without using potassium hydroxide and subsequent mild chemical activation. The hydrothermal carbonization was modified to study the effects of pH (5.92 and 10), temperature (200° and 240°C), and residence time (0.5 and 1 hour). The best-treated hydrochar were activated at 700°C for 1 hour to obtain superior mesoporous and microporous bio-adsorbents with a specific surface area of 339.92 m²/g. The bio-adsorbents were filled in a lab-scale fixed bed adsorber to test the adsorption of carbon-dioxide from 60% methane and 40% carbon-dioxide configured biogas. It was found that alkaline-based bio-adsorbent adsorbed 10.92% of CO₂ after 60 s test at 1 bar. The physicochemical properties of the hydrochar and bio-adsorbent were studied using proximate and elemental analysis, Thermo-Gravimetric Analysis (TGA), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) images, and Brunauer–Emmett–Teller (BET) analysis to distinguish the specific impact of the parameters and study the surface morphology.
DEDICATION

This thesis is dedicated to my:

Grandpa: Late Sujan Pradhan, Grandma: Binodini Pradhan

and

Mummy: Bindu Basini Garnaik, Papa: Kishore Chandra Garnaik

for their encompassing encouragement, care, and love so far.
ACKNOWLEDGEMENTS

Firstly, I would like to thank my advisor Dr. Animesh Dutta for his continuous supervision, and influential talks. His patience and open-door policy were immensely helpful to design my thesis throughout. I would also like to thank my committee member Dr. Rafael M. Santos for his kind support and with my writing skills. I would also thank Dr. Yi Wai Chiang for her valuable suggestions during the early stages of my research duration.

My acknowledgment is incomplete without expressing gratitude to Dr. Mahendra Thimmanagiri (OMA-FRA) and Dr. Ranjan Pradhan for their significant contributions in my work. Michael Speagle, Steve Wilson (Dept. of Physics), and Joanne Ryks thank you very much for helping me with my experimental setup and teaching on the usage of the laboratory equipment. I would like to express thanks to my BRIL members Zainab Al-Kabbi for designing the tubular reactor, Mohammad Heidari, Precious Arku, Shakirudeen Salaudeen, Eniola Adewakun, Dr. Subash Paul and Dr. Poritosh Roy. I’m grateful to my friends: Fatima, Khyati, Bhoomi, Adib, Faisal, and Sonika for making my journey much more comfortable.

Last but not the least, I would sincerely like to thank my brother Anshuman Garnaik, Anjali Pradhan (aunt), and my cousins Binjal, Unjal, Jahan, Tanishi, and Tasha for their endless love, advice, and counseling at my academic and personal level this far.
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<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>area_c</td>
<td>Area, m²</td>
</tr>
<tr>
<td>A_{N2}</td>
<td>Cross-section area of nitrogen (N₂), nm²</td>
</tr>
<tr>
<td>C</td>
<td>Constant for BET equation</td>
</tr>
<tr>
<td>C_{i}</td>
<td>Concentration of the iᵗʰ gas, mol/m³</td>
</tr>
<tr>
<td>conc_i</td>
<td>Concentration of CH₄, mol/m³</td>
</tr>
<tr>
<td>conc_ii</td>
<td>Concentration of CO₂, mol/m³</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer – Emmett – Teller</td>
</tr>
<tr>
<td>D</td>
<td>Diameter of the adsorber, m</td>
</tr>
<tr>
<td>D_{e,i}</td>
<td>Effective Diffusivity, m²/s</td>
</tr>
<tr>
<td>D_{i}</td>
<td>Diffusion coefficient, Diffusivity, m²/s</td>
</tr>
<tr>
<td>d_{p}</td>
<td>Diameter of the adsorbent particle, mm</td>
</tr>
<tr>
<td>(∂P/∂x)</td>
<td>Differential pressure drop, kPa/m</td>
</tr>
<tr>
<td>E₁, E₂</td>
<td>Molar adsorption energy for first layer and further layers during BET, J/mol</td>
</tr>
<tr>
<td>F</td>
<td>Degrees of freedom</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>k_{f}</td>
<td>Kinetic fluid particle mass transfer coefficient, m/s</td>
</tr>
<tr>
<td>k_{f}</td>
<td>Kinetic Freundlich constant</td>
</tr>
<tr>
<td>k_{L}</td>
<td>Kinetic Langmuir constant, g/mmol</td>
</tr>
<tr>
<td>k_{r}</td>
<td>Kinetic rate constant, min⁻¹</td>
</tr>
<tr>
<td>L</td>
<td>Length of the adsorber column, inch</td>
</tr>
<tr>
<td>LUB</td>
<td>Length of unused bed, m</td>
</tr>
<tr>
<td>LDF</td>
<td>Linear driving force</td>
</tr>
<tr>
<td>1/n</td>
<td>Slope for Freundlich log isotherm</td>
</tr>
<tr>
<td>n.a.</td>
<td>not available</td>
</tr>
</tbody>
</table>
\( N_A \) \hspace{0.5cm} \text{Avogadro’s number}  \\
\( N_B T \) \hspace{0.5cm} \text{Normal boiling temperature}  \\
\( N_i \) \hspace{0.5cm} \text{Flux of the i\textsuperscript{th} gas adsorbed}  \\
\text{PSA} \hspace{0.5cm} \text{Pressure swing adsorption}  \\
\text{ppm} \hspace{0.5cm} \text{parts per million}  \\
\( r_p \) \hspace{0.5cm} \text{Cylindrical pore radius, nm}  \\
\( r_K \) \hspace{0.5cm} \text{Kelvin pore radius, nm}  \\
\text{SEM} \hspace{0.5cm} \text{Scanning electron microscope}  \\
\text{STP} \hspace{0.5cm} \text{Standard temperature and pressure}  \\
\text{TGA} \hspace{0.5cm} \text{Thermogravimetric Analysis}  \\
\( \Delta Q \) \hspace{0.5cm} \text{Concentration gradient over an infinitesimally small distance, mol/m}^4  \\
\( Q_i \) \hspace{0.5cm} \text{Amount of the i\textsuperscript{th} gas adsorbed, mol/m}^3  \\
\( Q_{i,e} \) \hspace{0.5cm} \text{Equilibrium concentration capacity, mol/m}^3  \\
\( Q_{i,t} \) \hspace{0.5cm} \text{Concentration capacity at time ‘t,’ mol/m}^3  \\
\( Q_{\text{max}} \) \hspace{0.5cm} \text{Saturation loading capacity for the i\textsuperscript{th} gas adsorbed, mol/m}^3  \\
\( q_b \) \hspace{0.5cm} \text{BET multilayer adsorption capacity}  \\
\( q_{bm} \) \hspace{0.5cm} \text{BET monolayer adsorption capacity}  \\
\( q_{\text{sat}} \) \hspace{0.5cm} \text{Saturation loading for nitrogen, ml/g}  \\
\( u \) \hspace{0.5cm} \text{Uniform velocity, m/s}  \\
\( T \) \hspace{0.5cm} \text{Temperature, K}  \\

\textit{Greek Symbols}  \\
\( \rho \) \hspace{0.5cm} \text{Density, kg/m}^3  \\
\( \rho_g \) \hspace{0.5cm} \text{Density of gas, kg/m}^3  \\
\( \rho_{\text{NBP}} \) \hspace{0.5cm} \text{Density of liquid N}_2\text{ at NBT}  \\
\( \rho_{\text{STP}} \) \hspace{0.5cm} \text{Density of N}_2\text{ vapor at STP}  \\
\( \theta_p \) \hspace{0.5cm} \text{Bed porosity}  \\
(1 − \theta_p) \hspace{0.5cm} \text{Bed filling fraction}
K  Permeability, m$^2$
$\tau_f$  Tortousity factor
$\tau$  Tortoucity
$\mu$  Viscosity, (Pa-s)
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1 INTRODUCTION

1.1 Overview

Canada is the world’s fifth largest producer of natural gas and has a vast network of supply distribution pipelines (TransCanada Pipelines, 2018). With the on-going technological advancements in the extraction sites, the gas wells could supply one-third of Canada’s national energy requirements for another 300 years (CAPP, 2015; Faramawy et al., 2016). The global over-reliance on such non-renewable resources to produce energy is one of the most significant concerns of environmentalists, economists and power engineers (Tromly, 2001). The growing interest in developing and using alternative resources is a result of the following pressures: (i) ever-increasing energy demands due to the exponential rise of the global population that may cross 9 billion by 2040 (US Energy, 2017a), (ii) the spiking prices of gasoline/vehicular grade fuels in recent years and, (iii) the action taken for greenhouse gases (GHGs) mitigation, such as the Paris agreement of November 2016, which supports the implementation Carbon Capture, Utilization and Storage (CCUS) in the highest energy consuming developed and developing countries (Ham, 2008; IEA, 2016).

The conversion of biogas to renewable natural gas (RNG) or biomethane with a high content of methane is known as upgrading. The biomethane obtained after upgrading is compressed and delivered as liquified natural gas (Askari et al., 2015; Robins, 2013). It serves as an alternative solution to cope with the depleting reserves of natural gas and other fossil fuels. In Ontario, on-farm installations comprise 48% of Canada’s anaerobic digesters (AD) capacity, and few of them are delivering this ‘green fuel’ to natural gas distribution pipelines. In 2013, 37 biogas installations were operating on-farm in Ontario with 51 other projects under development (Bradburn, 2014;
DeBruyn and Hilborn, 2015). The most abundant feedstock to these digesters are biomass such as discarded parts of energy crops (corn silage, hay, and grasses), other agricultural waste, oils, and greases from urban centers, and beef and potato rejects (Abatzoglou and Steve, 2009). However, according to Kajat (2006), dozens of sites in Canada generate biogas from landfills that are directly burnt off to produce electricity. European nations are leading with the highest number of biogas plants, i.e., over 17,200 that are focusing on the production of vehicular grade fuel (European Biogas Association, 2015). As of January 2015, there were 247 livestock anaerobic digesters (AD), 645 operative landfills and 1,500 wastewater treatment plants (WWTP) producing biogas in the United States (Shen et al., 2015). However, most of these sources deliver electrical energy rather than vehicular fuel (US Energy, 2017b). Many developing countries have been using biogas as a source of cooking fuel (Kadam and Panwar, 2017), but this untreated biogas cannot be used directly as a high-grade vehicular fuel or in combined heat and power (CHP) industries (Singhal et al., 2017). Even though intensification of biochemical and thermochemical processes at digester and reactor levels, respectively, has maximized the methane recovery, still, upgrading remains as an inevitable step.

Pressure swing adsorption (PSA) and high-pressure water scrubbing (HPWS) are industrially operative around the world to perform the upgrading of biogas to achieve the RNG specifications. HPWS is widely used to upgrade the biogas generated from WWTPs in North America due to the high availability of water resources. A significant problem associated with this method is high consumption of water as the absorbent/solvent to capture CO₂, and this causes exhaustion of an essential natural resource. In addition to this, there is a demand for energy to dry the product gas in the subsequent stages (Nock et al., 2014). Sun et al. (2015) have mentioned that conventional
PSAs requires much attention to the CH$_4$ losses and H$_2$S removal. Additionally, there is a dilemma in choosing adsorbent for improving efficiency in PSA. The factors considered for selection of the adsorbent for upgrading biogas to eliminate maximum undesirable components are: (i) high separation efficiency; (ii) easy regeneration capacity; and (iii) cost-effectiveness. Within the last five years, significant efforts have been made to transform bio-waste into mesoporous and nanoporous adsorbents by applying carbonization and other activation techniques that enhance adsorption capacity and selectivity. Even though there has been extensive reaction kinetics research and adsorption studies on biomass-based adsorbents, limited work has been done in verifying their performance in the pre-treatment steps, and in PSA for CH$_4$/CO$_2$ separation, for biogas upgrading. Although in the hybrid approaches like a combination of PSA and HPWS, or PSA and membrane separation, results in high purity CH$_4$ and high recovery, it adds to the operative and installation costs. Figure 1 presents an overview of the biogas industry that starts from the generation stage in ADs, WWTPs, and landfills followed by several treatment and purification steps to produce the final product as biomethane and its utilization.
1.2 Scope and Objectives

1.2.1 Problem statement
The Ontario Ministry of Environment and Climate Change invested $100M in fighting climate change by enforcing reduction of GHGs (15% by 2020) and create employment opportunities sustainably over a period of four years (2016-2020). The Ontario Ministry of agriculture, food, and rural affairs. The agricultural and food waste are currently being diverted towards the generation of RNG (OCE, 2018). However, industrial upgrading processes require low-cost adsorbents to capture CO₂ from these methane-rich streams. Prolonged carbonization (pyrolysis) followed by extreme conditions for activation of biomass is suggested as the most efficient way to produce activated carbon. The change in physicochemical properties, as well as the surface morphology, contributes to the synthesis of highly nanoporous adsorbent. However, it consumes an enormous amount of energy, chemicals/activating agent, time that makes them expensive when
compared to zeolites. Thus, in this study, low-temperature pre-treatment by hydrothermal means (with and without alkaline solvent) and, mild chemical activation of the hydrochar obtained is studied to be a better alternative for the selective separation of CO\textsubscript{2}/CH\textsubscript{4} streams.

1.2.2 Research Objectives

The primary objective of this work is to understand the bio-adsorbent properties of relativity to the separation of CO\textsubscript{2} from the methane-rich streams. It was compared to a commercial adsorbent to calculate its efficiency in terms of \( x \) mmol of CO\textsubscript{2}/ g of bio-adsorbent. The research areas are:

1. Investigate the change in physicochemical properties and mass yield with respect to the hydrothermal pre-treatment method used. The parameters considered for the hydrothermal processes were reaction time, pH of the solvent, and temperature. The physicochemical properties were studied based on the proximate and elemental analysis, Thermo-Gravimetric Analysis (TGA), and Fourier-Transform Infrared Spectroscopy (FTIR).

2. Selection of the different types of hydrochar as the feedstock for activation process and determining the structural changes using SEM and BET analysis and other physicochemical properties associated.

3. Designing the fixed-bed adsorption column to examine the bio-adsorbent produced in terms of the effect of pressure and gas residence time on adsorption kinetics under isosteric conditions.

4. Modeling the adsorption kinetics using Freundlich and Langmuir’s kinetics theory to validate the experimental results.
1.2.3 Research Methodology

The procedure designed for this study is shown in Fig.1.2. In Switchgrass fines (bio-waste) was studied to investigate the potential for developing bio-adsorbent. The results after the hydrothermal pre-treatment and alkaline hydrothermal pre-treatment were compared to procure the feedstock for the activation process. The hydrochar was then charged with mild chemical (alkaline) activation to produce the bio-adsorbents. The later obtained products were used in a fixed-bed adsorber to evaluate the separation efficiency in terms of CO$_2$ loading and CH$_4$/CO$_2$ final compositions.
Figure 1.2 Flowchart of the presented thesis research methodology
1.3 References


2 LITERATURE REVIEW

The research topics were categorized into three major areas: (i) biomass conversion efficiency to produce biogas in the digesters; (ii) maximizing the CH$_4$ concentration by using bio-adsorbents to remove undesirable components; and (iii) exploring pioneering ways to produce bio-adsorbents using bio-waste. The authors weighed the upgrading techniques in the text based on the 1-5 criterion scale. The subsequent in-depth search for each of the topics resulted in over 150 references within the context of the review.

The most crucial step of this review was extracted from the details of the text such as:

- On-going research efforts to improve methane conversion, and comparison of outcomes from the selected works;
- Morphological structure of the adsorbents to suit the adsorption of the contaminants in the biogas;
- Environmental and economic factors that affect the upgrading processes; and
- Evaluating the potential of the bio-waste to produce bio-adsorbents for industrial pressure swing adsorption (PSA) systems.

2.1 Measures and Challenges in Biogas Generation

There are three major contributors to the GHG emissions, i.e., ADs, WWTPs, and landfills which are significantly rising with the amount of waste generated around the globe. In Ontario, Canada, the feedstocks to the ADs mainly constitute of organic waste matter obtained from agricultural farms, food wastes, energy crops, (Bradburn, 2014). These feedstocks are broken down in the digesters by micro-organisms into simple compounds such as CH$_4$ and CO$_2$, in the absence of O$_2$, with a solids retention time (SRT) of 3-20 days under optimum operating conditions of pH range
within 6.5-7.5 and temperature of 35-38°C (Busch, 2013; Wang et al., 2018). However, the challenges cited by various researchers for efficient enrichment of biogas to appropriate grade of natural gas are associated with the initial conversion of organic matter via anaerobic methods at the ADs.

2.1.1 Anaerobic Fermentation/Digestion

The on-farm ADs in Ontario run on feedstocks such as manure do not produce siloxane (Si-O-Si) compounds, which eliminates the required step for removing them (Robins, 2013). However, in the 1980s these ADs failed due to issues while operating and thus were found not to be economically feasible (DeBruyn and Hilborn, 2015). Since countries in the Northern hemisphere have a cold climatic condition, a significant challenge to operating the digesters is providing thermal insulation for maintaining the optimum temperature. Thus, it increases the overall energy consumption and operational costs.

Nielsen et al. (2009) identified that regulation of the most critical parameters during this biological process, such as temperature, organic loading rate, hydraulic and solid retention time, Carbon:Nitrogen (C/N) ratio and pH, will enhance the biogas yield. The process of purifying and enriching biogas to RNG from anaerobic digestion of waste generates additional solid residues that are beneficial for plant growth in agricultural applications, and pre-digesting these wastes minimize the emissions of \( \text{CH}_4 \) emissions into the atmosphere after the application into the soil. Harris et al. (2008) listed some of the microbial and chemical factors influencing methanogenesis using low-ranked subsurface coal (which comprises about 60% of the total United States reserves), such as hydrolytic depolymerization of organic material, enzymatic activity of microbes,
consumption of H$_2$/CO$_2$ or acetates by methanogens, and the intraspecific competition against homoacetogens. This study provides evidence that by controlling the parameters mentioned above, the anaerobic digestion of biochar, similar to low-ranked subsurface coal, can increase CH$_4$ recovery. Panjičko et al. (2017) used brewery spent grain in the two-stage anaerobic digestion process that enhanced hydrolysis and acidogenesis in a solid-state digester, and methanogenesis in a granular biomass reactor. The results showed an efficient total solids degradation up to 83%. For commercial digesters, the feed is usually a mixture of various types of wastes. Thus, it undergoes the co-digestion process.

Recent developments in anaerobic fermentation (AF) have found another source to obtain biogas, namely lignocellulosic biomass, wherein the hemicellulose and cellulose present in this biomass are converted into CH$_4$ and CO$_2$. However, this method requires pretreatment to convert the compact structure of the lignocellulosic biomass into simpler carbohydrates (Bong et al., 2018; Dahunsi et al., 2017). Some of the pre-treatment methods include using acidic, alkaline, chemicals, hot water or steam explosion methods (Kim, 2013). Pobeheim et al. (2011) studied the impact of heavy metals (nickel and cobalt) on AF of maize silage model substrate. They found that with an organic loading rate of up to 4.3 g·L$^{-1}$·d$^{-1}$ of organic dry mass, the fermentation process was stable in the presence of the metal ions, which up to specific metal loadings aided in biogas production. Wang et al. (2015) compared two-stage anaerobic fermentation of rice straw using NaOH (2%) and HCl (1%) pre-treatment and studied the effect of hydrolysate concentration on the improvement of biogas production. The digestion of hydrolysate after acidic treatment enhanced the CH$_4$ recovery by nearly 44%. During two-stage AF of 400 g of corncob, Li et al. (2015)
combined black soldier fly larvae to the process to produce 86.7 L of biogas and 3.17 g of biodiesel from the digestate.

2.1.2 Catalytic Gasification

The natural ways to produce biogas and further upgrade is a long process; researchers suggested a non-biological, thermochemical method to ultimately produce biogas is via catalytic gasification followed by Sabatier’s reaction (Lange et al., 2018). Although it is an energy-intensive process, the integration of syngas (H₂ and CO) production and methanation has led to the faster production of RNG. The biomass, typically wood, is gasified in the presence of air/oxygen and steam at a temperature of 850°C and converted into producer gas, which primarily consists of syngas. It is further processed to remove tar, sulfur, and chlorides with simultaneous cooling (Chynoweth et al., 2001). The cooled producer gas transforms into CH₄, CO₂, and H₂O upon methanation reaction in the presence of nickel catalyst (Baeyens et al., 2016; Turco et al., 2016; Meijden et al., 2011). However, the formation of non-flammable gases (N₂ and CO₂) and catalyst poisoning caused by sulfur and carbon depositions are some of the challenges that need to be resolved to achieve maximum conversion. In the syngas process, common catalyst materials are cobalt, iron, and ruthenium, as nickel is known to promote methane formation (Rauch et al., 2014).

2.1.3 The need for upgrading

The primary challenge to use untreated raw biogas for vehicular-grade fuel or power generation applications is the presence of contaminants. These undesirable components are carbon dioxide (CO₂), hydrogen sulfide (H₂S), water vapor (H₂O), volatile organic compounds (VOCs), siloxane (Si-O-Si) compounds, ammonia (NH₃), halides, hydrogen (H₂), and oxygen (O₂) (Lijó et al., 2014).
Table 1. lists the composition of biogas produced from various methods, and it can be noted that the Higher Heating Value (HHV) of untreated raw biogas should be nearly double so that it can be used consistently as a substitute for natural gas (NG). These processes not only achieve the required grade of fuel but also generate highly pure CO$_2$ that can be used: (i) as a source to activate the biochar obtained after carbonization process physically; (ii) in chemical industries to produce other chemicals and materials; (iii) as a gasifying agent in gasification of biomass; (iv) Enhanced Oil Recovery; or (v) in CO$_2$ sequestration.
<table>
<thead>
<tr>
<th>Component</th>
<th>Units</th>
<th>AD</th>
<th>Landfills</th>
<th>WWTP</th>
<th>Natural Gas Pipeline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Nahar et al., 2017; Mamun et al., 2017; Rasi et al., 2007)</td>
<td>(Nahar et al., 2017; Rasi, 2009)</td>
<td>(Wheeldon et al., 2007; Rasi, 2009)</td>
<td>(Enbridge Gas Distribution, 2018; TransCanada Pipelines, 2018)</td>
</tr>
<tr>
<td>CH₄</td>
<td>m³</td>
<td>0.53-0.70</td>
<td>0.30-0.65</td>
<td>0.58-0.70</td>
<td>0.9321</td>
</tr>
<tr>
<td>CO₂</td>
<td>m³</td>
<td>0.30-0.50</td>
<td>0.25-0.47</td>
<td>0.30-0.43</td>
<td>0.0054</td>
</tr>
<tr>
<td>N₂</td>
<td>m³</td>
<td>0.02-0.06</td>
<td>&lt; 0.01-0.17</td>
<td>0.012-0.071</td>
<td>0.0101</td>
</tr>
<tr>
<td>O₂</td>
<td>m³</td>
<td>0-0.05</td>
<td>&lt; 0.01-3</td>
<td>0.001-0.02</td>
<td>0.004 (permissible)</td>
</tr>
<tr>
<td>H₂</td>
<td>m³</td>
<td>n.a.</td>
<td>0-0.03</td>
<td>0-0.0001</td>
<td>n.a.</td>
</tr>
<tr>
<td>Light hydrocarbons</td>
<td>m³</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.0524</td>
</tr>
<tr>
<td>H₂S</td>
<td>ppm</td>
<td>0-2000</td>
<td>30-500</td>
<td>2.5-3450</td>
<td>23 mg/m³ (permissible)</td>
</tr>
<tr>
<td>NH₃</td>
<td>ppm</td>
<td>&lt; 100</td>
<td>0-5</td>
<td>&lt; 1</td>
<td>n.a.</td>
</tr>
<tr>
<td>Total Chlorides</td>
<td>mg/m³</td>
<td>&lt; 0.25</td>
<td>0-225</td>
<td>&lt; 0.1</td>
<td>n.a.</td>
</tr>
<tr>
<td>Siloxanes</td>
<td>ppm</td>
<td>&lt; 0.08-0.5</td>
<td>&lt; 0.3-36</td>
<td>0-2500</td>
<td>n.a.</td>
</tr>
<tr>
<td>H₂O</td>
<td>m³</td>
<td>0.06</td>
<td>n.a.</td>
<td>0.0001</td>
<td>65 mg/m³ (permissible)</td>
</tr>
<tr>
<td>VOCs</td>
<td>mg/m³</td>
<td>5-8</td>
<td>46-173</td>
<td>13-268</td>
<td>n.a.</td>
</tr>
<tr>
<td>HHV</td>
<td>kWh/m³</td>
<td>6.388 (calculated)</td>
<td>4.444 (calculated)</td>
<td>6.722 (calculated)</td>
<td>10.778</td>
</tr>
</tbody>
</table>

considering the basis of biogas volume = 1 m³; ppm = parts per million; mg/m³ = milligrams per m³
n.a. - not available
Contaminants in biogas are harmful to CHP engines due to their corrosive nature. Table - 2.1 lists some of the problems associated with each of the undesirable components present in the raw biogas stream and the methods to remove them. The temperature of raw biogas generated from the ADs, WWTPs or landfills is nearly 40°C, therefore contains much moisture. When it passes through pipelines at the ambient temperature of a colder climatic region (~0°C), it tends to lose moisture naturally by condensation. This turns out to be favorable when practiced on a large scale. In addition to natural condensation, installation of a column with hygroscopic salts will help to maximize the removal efficiency of water vapor from biogas. At the farm sites, passing the biogas in columns filled with ferrous-oxides is one of the most efficient ways to remove H$_2$S. However, these spent metal-oxides are a concern to environment/soil health management due to its disposal on open grounds. The current technologies have been able to eliminate H$_2$S, water vapor, and NH$_3$ during the pre-treatment stages that include chemical absorption, drying, and physical adsorption on activated carbon, thus resulting in biogas composition satisfactory for the further upgrading processes (Mamun et al., 2015).
<table>
<thead>
<tr>
<th>Component</th>
<th>Problem</th>
<th>Method of Removal*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Lower Heating value</td>
<td>PSA, HPWS, Membrane separation, Cryogenic distillation, ESA, TSA, Chemical absorption, Physical scrubbing, Membrane absorption</td>
<td>(Niesner et al., 2013)</td>
</tr>
<tr>
<td>H₂O</td>
<td>Corrosion, Rust, Washes away lubrication</td>
<td>Drying, Chillers, Compression, Silica gel, Hygroscopic salts such as – CaO and Na₂SO₄, Molecular Sieves, Activated Carbon.</td>
<td>(Mamun et al., 2015)</td>
</tr>
<tr>
<td>H₂S</td>
<td>Unpleasant odor, leads to the formation of SO₂ and H₂SO₄, Toxic to adsorbents of PSA</td>
<td>Chemical Absorption, activated carbon, Fe-Chelate method, Reaction with FeCl₂, Fe₂O₃, Biological treatment in digesters</td>
<td>(Mamun et al., 2015; Horikawa et al., 2004)</td>
</tr>
<tr>
<td>NH₃</td>
<td>Forms nitrogen oxides during combustion in gas engines, Foul odor</td>
<td>Acidic solvent-based gas-scrubbing</td>
<td>(Abatzoglou and Steve, 2009)</td>
</tr>
<tr>
<td>N₂ and O₂</td>
<td>Lowers heating value, Corrosion</td>
<td>Adsorption on activated carbon, molecular sieves, membranes</td>
<td>(Persson et al., 2006)</td>
</tr>
<tr>
<td>Siloxanes</td>
<td>Abrasion of engines, insulators, and plugs</td>
<td>Cooling, Scrubbing with organic solvents, Chemical Adsorption with activated carbon, Silica gel</td>
<td>(Korres, 2013)</td>
</tr>
<tr>
<td>Halides</td>
<td>Forms corrosive acids (HCl, HF), Increases frequency to change engine oil</td>
<td>Adsorption on activated carbon at 200°C</td>
<td>(Korres, 2013)</td>
</tr>
</tbody>
</table>
Adsorption on activated carbon is the most commonly employed method for contaminant removal, according to Table 2.2, and thus can be potential adsorbent for the industries working with PSA units.

In British Colombia, Canada, Xebec Inc., have installed PSAs to upgrade biogas from the ADs that have proven to be 96% efficient. With 99.8% CH4 recovery, they have also installed high-performance polymer membrane separators in China and North America (Xebec Adsorption Inc., 2015). HPWS is a separation technology that falls under the category of physical absorption (Niesner et al., 2013). In this process, the pressurized biogas (6-12 bar) is pumped in a countercurrent direction to the water that scrubs CO2 out of the system in dissolved form. This stream of dissolved CO2 and water passes into a regenerative column at low pressure that releases the captured CO2, and the water is recycled back into the system (Chandra et al., 2012). In Hamilton, Ontario, Flotech Inc. operates a water scrubber with a capacity of about 10,000 Nm³/h (10,592 m³/h at STP) to enrich biogas from WWTP (Greenlane and Flotech, 2011).

Molino et al. (2015) developed a method to produce biomethane at low pressures by using a smart grid injection method. They used polymeric membrane module and operated it at a pressure ranging from 2-15 bar. They found the purity varied from 60-93% at the expense of decreasing CH4 recovery from 98% to 70%. Grande et al. (2009) studied another CO2 capturing method known as electric swing adsorption for post-combustion flue gas cleaning. It can be inferred that this technique can be used to upgrade biogas. However, it is an energy-intensive process. Since pretreatment stages consume additional energy, a synergistic approach was studied to overcome the challenges of upgrading biogas economically and removing maximum contaminants in a single step. A lab-scale packed bed reactor was designed by Kashikaphaiboon et al. (2013) that used
MEA (monoethanolamine), calcium and sodium hydroxide solutions to scrub over 90% of both CO₂ and H₂S efficiently. Recently developed second-generation upgrading technologies are more efficient (~99%) but are dependent on high energy requirements in the form of steam or heat, pressure, cryogenic cooling, and electricity. These aspects add onto the operating expenses; thus, industries currently prefer mainly PSA (the focus of the next section of this review), together with wide dissemination of water and amine scrubbing (Ryckebosch et al., 2011; Sun et al., 2015; Bauer et al., 2013). Table - 2.3 lists and briefly describes the available technologies to purify biogas and derive RNG. The scoring mentioned in the Table - 2.4 is calculated based on the following factors. Each of the factors carries one point. For a few techniques, if data not available the total score is calculated as in equivalent of five.

1. Efficiency: This criterion is considered of the highest impact for any process to be evaluated. If maximum literature cites that average upgrading is >95%, the process gets a full score - 1/1; 90-95% - 0.5/1; <90% - 0/1

2. Energy consumption: The mechanisms of the upgrading processes require energy in the form of mechanical (compressors and pumps)/electrical/heat. PSA works on heavy usage of mechanical compression energy and equivalent electric demand but only gives to a total of 0.23-0.3 kWh (Bauer et al., 2013). However, if there is a supplementary requirement of any form of energy other than compression for any other process, the score decreases by 0.5. If the process consumes very high energy when compared to PSA, it gets 0/1.

3. The requirement of additional chemicals: If no then 1/1; if low-cost 0.5/1; if expensive 0/1

4. The requirement of additional steps: If yes then 0/1; or else 1/1
5. Ease of the operation: If too complicated when compared to PSA, then 0/1; if moderately then 0.5; or else 1/1
Table - 2. 3 Overview of competitive processes to upgrade biogas

<table>
<thead>
<tr>
<th>Methods</th>
<th>Description</th>
<th>Efficiency (%)</th>
<th>Energy consumption (kWh/m³ at STP)</th>
<th>Usage</th>
<th>Score</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Absorption (HPWS)</td>
<td>Solvent, i.e., water, scrubs the highly dissolvable CO₂ at high pressure, and the solvent are regenerated by depressurizing. H₂S removal is not necessary prior to this upgrading technique. Higher CH₄ slip.</td>
<td>88.9-96</td>
<td>0.24-0.95</td>
<td>As HPWS.</td>
<td>3/5</td>
<td>(Ray et al., 2014; Nock et al., 2014)</td>
</tr>
<tr>
<td>Organic solvent scrubbing</td>
<td>Poly-ethyl glycol esters and other commercial organic solvents have higher affinity to dissolve CO₂. The used solvent is renewed by heating at 55-80°C. H₂S removal is necessary before this scrubbing technology.</td>
<td>90-95.5</td>
<td>0.21-0.71</td>
<td>Limited due to high installation costs and the solvents are corrosive.</td>
<td>2/5</td>
<td>(TUV, 2012)</td>
</tr>
<tr>
<td>Membrane Separation</td>
<td>Selective gas permeation. The semi-permeable membrane allows CO₂ to pass as off-gas and CH₄ stays as retentate. Highly intensified technology with operating pressures of 8 – 20 bars.</td>
<td>82.4-98</td>
<td>0.16-0.46</td>
<td>Mostly European.</td>
<td>4/5</td>
<td>(Micale, 2015; Favre et al., 2009)</td>
</tr>
<tr>
<td>Chemical Scrubbing</td>
<td>Potassium Arginate, mono-, di-, tri-ethanolamine reacts specifically with CO₂. High CH₄ recovery. The solvent requires high temperature (120-170°C) to regenerate.</td>
<td>88.5-97.7</td>
<td>0.11-1.59</td>
<td>As amine scrubbing.</td>
<td>1.5/5</td>
<td>(Abdeen et al., 2016; Leonzio, 2016)</td>
</tr>
<tr>
<td>Cryogenic Separation</td>
<td>Based on the freezing point of CO₂ (~ -110°C). CO₂ condensed out from biogas and 98% pure CH₄ is obtained. High pressure (200 bar) compression of biogas consumes a lot of energy.</td>
<td>84.9-96.7</td>
<td>0.21-1.63</td>
<td>Limited as it is energy intensive.</td>
<td>2/5</td>
<td>(Yousef et al., 2016; Petersson and Wellinger, 2009)</td>
</tr>
<tr>
<td>Technique</td>
<td>Description</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Limited as it is energy intensive</td>
<td>3.75/5</td>
<td>References</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
<td>------</td>
<td>-----------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>TSA</strong></td>
<td>In PSA, the desorption of gases occurs at low pressure, but in TSA it happens at high temperature (120°C). Shortens the duration of the cycle.</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
<td>(Yang, 2003; Luo, 2013)</td>
</tr>
<tr>
<td><strong>Hybrid membrane techniques</strong></td>
<td>Some examples are membrane absorption, TSA followed by a membrane, etc. These are process-intensified techniques when compared to the conventional methods to obtain high purity CH₄.</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
<td>(Shao et al., 2012; Zhang et al., 2014)</td>
</tr>
<tr>
<td><strong>Biological enrichment</strong></td>
<td>Methanation using chemo-autotrophic and sulfur-reducing bacteria and creating a most favorable environment for the microorganisms.</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
<td>(Li et al., 2015)</td>
</tr>
<tr>
<td><strong>Gas Hydration</strong></td>
<td>Using phase change, gas hydration is a combined method of H₂S and CO₂ removal that optimizes energy consumption. These are crystalline solids that are formed by Van der Walls force bonding to water molecules. High pressure (40-60 bar) operation and an exothermic process with internal temperature maintained at 3°C. Requires multi-stage operation for maximum purity.</td>
<td>92%</td>
<td>3.8-3.9% as specific energy consumption</td>
<td>Emerging technology</td>
<td>1.5/5</td>
<td>(Filarsky et al., 2018) (Castellani et al., 2014)</td>
</tr>
</tbody>
</table>

n.a. – not available; * - cannot be scored since all values are indicators of the type of a hybrid technique used; ** - cannot be scored since all values are unavailable
Table - 2.4 Score chart of the competitive processes

<table>
<thead>
<tr>
<th>Methods</th>
<th>Efficiency</th>
<th>Energy consumption</th>
<th>Additional chemical</th>
<th>Additional steps</th>
<th>Ease</th>
<th>Total score</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPWS</td>
<td>0.5</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Organic solvent scrubbing</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Membrane Separation</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Chemical Scrubbing</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cryogenic Separation</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>TSA</td>
<td>-</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>$\frac{3}{4} = 3.75/5$</td>
</tr>
<tr>
<td>Gas Hydration</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
</tbody>
</table>
2.2 Pressure Swing Adsorption

2.2.1 Working Principle

PSA is a conventional separation technique used to adsorb CO$_2$ on a solid porous adsorbent at high pressures, operated cyclically and repetitively. This method includes pressurizing the feed as well as the upgraded product streams, followed by high-pressure adsorption of the gases, pressure equalization, blow-down to depressurize the column to desorb CO$_2$ and simultaneously regenerate the adsorbents, and low-pressure purging. The sequence is represented in Figure 2.1. PSA is an established technology that works on the Skarstrom cycle based on the principle of physisorption (Knaebel and Hill, 1985). Grande (2011) has explained the sequential stages about the working of a PSA cycle based on a modified Skarstrom cycle. Skarstrom cycle denotes PSA as a two-step process that involves adsorption at high pressure and regeneration/desorption by lowering the pressure, but Yang (2003) describes a modified process that results in the loading of CH$_4$ per cycle to be constant, which is called a cyclic steady state (CSS). It also results in better productivity and minimizes the energy consumption to re-pressurize the feed. The following described this multi-step PSA process:

(a) High-pressure adsorption step: In the first stage, the pretreated biogas (PT-biogas) is pressurized and fed at the 6-8 bar of high pressure. The adsorption of CO$_2$ is initiated on the adsorbent, and the CH$_4$-rich stream (biomethane) is collected as a product or used as purge gas in another column.

(b) Depressurization equalization step (EQ2): The pressurized gas present in the interstitial spaces at the end of the column exits in the co-current direction and partially pressurizes another column.
(c) Depressurization blowdown (BD) step: It succeeds the EQ2 stage until the pressure goes down to nearly vacuum conditions.

(d) Re-pressurization equalization step (EQ1): It occurs in the second column, which is receiving the gas that leaves the first column during the EQ2 step, thus making the second column partially pressurized and reducing the compressor energy consumption to pressurize the column to 6-8 bar.

(e) Final regeneration purge step (PU): Biomethane flows in counter-current direction through the de-pressurized column to purge out impurities (CO₂) to the off-gas stream. The pressurized PT-biogas then enters the purged unit as feed, and with this, the cycle continues the initial phase as described in the first stage (a).

Figure 2. 1 Multi-column PSA based on modified Skarstrom cycle (Khan et al., 2017). Reprinted with permission from Elsevier (license 4325100397784)
2.2.2 Design considerations

The adsorbent is the crux of this process, and its selective adsorption performance to capture CO$_2$ from the pre-treated biogas (PT-biogas) enables conversion to biomethane. The operational expenses include the cost of changing the degraded adsorbents after several years, along with the mechanical energy expended in the compression of the feed (Abatzoglou and Steve, 2009). There are different types of configurations available based on different types of adsorbents used, several cycles and the design of adsorption columns to obtain $\geq$99% pure biomethane, but the most commonly employed is the two-column configuration with packed beds (Grande, 2012). The selected adsorbent is filled in the central zone of the columns with a void fraction of nearly 78% for maximum CO$_2$ capture (Grande, 2011).

2.2.3 Modeling a PSA unit

With the help of a dynamic non-isothermal model based on linear driving force (LDF) and approximation of mass transfer with a single lumped transport parameter ($k_{\text{LDF},i}$), the kinetics of the adsorption process can be described. The model of a PSA is based on the following assumptions:

i. The gases follow axially dispersed plug flow and ideal gas behavior;

ii. There is no radial concentration and temperature gradients. Thus, thermal equilibrium is maintained between solid and gas phases; and

iii. There is an adiabatic interaction with surroundings.
The system is solved according to a set of partial differential equations. Agarwal (2010) mathematically modeled and designed a PSA using gPROMS software. The experimental setup by Lestinsky et al. (2015) as well as the numerical modeling by Agrawal suggests that high purity CH$_4$ (98%) and recovery of 80% can be obtained with a single PSA unit. Augelletti et al. (2017) modeled the most recent configuration of the upgrading process that takes place in four interconnected columns and produces biomethane. They suggested that recovery can be as high as 99% with minimum energy consumption of 1250 kJ/kg of biomethane. It was also confirmed that the CH$_4$ slip/losses are minimum with PSA (< 2%). Vemula et al. (2015) modeled rapid PSA using COMSOL Multiphysics and MATLAB software for separation of N$_2$/He feed mixture on zeolite-5A. Rapid PSA is the time-based intensification of the conventional PSA. They considered functional adiabatic adsorber properties and found 99.9% pure helium could be obtained in 5.5 s. This development can be implemented to separate CH$_4$/CO$_2$ mixtures at a faster rate.

Some of the PSAs used for CH$_4$/CO$_2$ streams are listed in Table 2.5. The performance of PSA can be calculated by evaluating: (i) purity of CH$_4$ obtained in the product; (ii) recovery of CH$_4$ after the purge step; and (iii) productivity of a unit for the adsorbent used and time taken to complete one cycle (Grande, 2011).
Table 2.5: Types of PSAs known to separate a CO2/CH4 mixture

<table>
<thead>
<tr>
<th>Type of PSA</th>
<th>Feed</th>
<th>Feed Pressure (bar)</th>
<th>Feed Temp. (°C)</th>
<th>Adsorbent used</th>
<th>Total no. of cols.</th>
<th>% CH4 purity</th>
<th>% CH4 recovery</th>
<th>Time (s)</th>
<th>Productivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 – bed &amp; 4 – steps</td>
<td>55% CH4 45% CO2</td>
<td>3.2</td>
<td>31-35</td>
<td>CMS – 3K</td>
<td>1</td>
<td>97.1</td>
<td>79.4-86.3</td>
<td>400</td>
<td>n.a.</td>
<td>(Grande, 2011)</td>
</tr>
<tr>
<td>4 – bed &amp; 9 – steps</td>
<td>67% CH4 33% CO2</td>
<td>4</td>
<td>50</td>
<td>CMS – 3K</td>
<td>4</td>
<td>97.88-98.3</td>
<td>88.5-88.93</td>
<td>900</td>
<td>5.5</td>
<td>(da Silva Santos et al., 2011)</td>
</tr>
<tr>
<td>Duplex PSA</td>
<td>55% CH4 45% CO2</td>
<td>2-4</td>
<td>25</td>
<td>Zeolite 5A</td>
<td>95-99</td>
<td>n.a.</td>
<td>2-5.5</td>
<td>1.3</td>
<td>(Thakur and Kaistha, 2011)</td>
<td></td>
</tr>
<tr>
<td>Vacuum PSA 5-steps</td>
<td>55% CH4 45% CO2</td>
<td>6-8</td>
<td>33</td>
<td>CMS-3K</td>
<td>1</td>
<td>98.1</td>
<td>79.7</td>
<td>400</td>
<td>3.83</td>
<td>(Shen et al., 2011)</td>
</tr>
<tr>
<td>Vacuum PSA 5-steps</td>
<td>55% CH4 45% CO2</td>
<td>6-8</td>
<td>33</td>
<td>Zeolite – 13X</td>
<td>1</td>
<td>96.58</td>
<td>48.6</td>
<td>400</td>
<td>3.20</td>
<td>(Grande and Rodrigues, 2007a)</td>
</tr>
<tr>
<td>Layered VPSA 5-steps</td>
<td>55% CH4 45% CO2</td>
<td>8</td>
<td>n.a.</td>
<td>CMS – 3K and Zeolite – 13X</td>
<td>2</td>
<td>98.0</td>
<td>60.1</td>
<td>400</td>
<td>7.24</td>
<td>(Grande and Rodrigues, 2007b)</td>
</tr>
<tr>
<td>Layered PSA</td>
<td>30-45% CO2</td>
<td>8</td>
<td>25</td>
<td>CMS-3K and Zeolite – 13X</td>
<td>2</td>
<td>98.7</td>
<td>74.8</td>
<td>400</td>
<td>2</td>
<td>(Grande et al., 2008)</td>
</tr>
<tr>
<td>28-bed Kinetic Rotary PSA</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Zeolite molecular sieves or, CMS</td>
<td>1</td>
<td>97-99</td>
<td>95-99</td>
<td>2</td>
<td>n.a.</td>
<td>(Alizadeh-Khiavi et al., 2013)</td>
</tr>
</tbody>
</table>
2.3 Adsorbents

Adsorption is an exothermic separation phenomenon whereby a solid porous medium (adsorbent) adsorbs physically/chemically a component (adsorbate) to be separated (Yang, 2003). Recently, low-cost adsorbents are primarily of interest for industrial applications (Kambo and Dutta, 2015). The efficiency of the upgrading and pre-treatment requirements are based on the selection of adsorbent. Many researchers have experimented CO$_2$ capture in PSA using carbon-based zeolites, MOFs (metal organic frameworks) and functionalized silica adsorbents, but the most effective has typically been found to be carbon-based adsorbents (Grande et al., 2005; Kwaśny and Balcerzak, 2016; Alonso-Vicario et al., 2010). Some of the commonly used carbon-based adsorbents in PSAs are activated carbon (AC), and carbon molecular sieve (CMS-3K and CMS-5A).

The International Union of Pure and Applied Chemistry (IUPAC) classifies adsorbents based on the pore morphology and size, i.e., microporous (>50 nm), mesoporous (2-50 nm), and nanoporous (<2 nm) adsorbents (Do, 1998). Also, adsorbents can be broadly classified into two categories based on adsorption mechanism: equilibrium- and kinetics-based (Grande and Rodrigues, 2007a). On the surface of kinetic-based adsorbents, the adsorption occurs due to the kinetics of chemisorption reaction according to the Freundlich or Langmuir models (Lau et al., 2016). The equilibrium-based adsorbents work on the physisorption isotherms, which become unstable after a few cycles (Hicks et al., 2008). Bagreev et al. (2001) have studied the kinetics of both types of adsorption and found that chemisorption is more efficient than physisorption, but the regeneration of spent kinetics-based adsorbents consumes a high amount of energy.
2.3.1 Activated carbon

AC is the most widely used adsorbent for various industrial applications due to the high specific surface area (>300 m²/g), high porosity (0.2-2 cm³/g), nominal bulk density (~450 kg/m³), abrasion resistance, and known capacities for gas and wastewater purification properties. AC is considered as an adsorbent in the pre-treatment step and in the PSA process for biogas upgrading. Highly developed twisted pores (tortuosity), ability to withstand repetitive use and low cost are some more factors to consider while selecting the adsorbent for prolonged industrial applications. Also, the specific heat capacity also plays an essential parameter to select an adsorbent for a specific process (Knaebel, 2008). Other carbon-based adsorbents such as carbon molecular sieves (CMS), monolithic carbon, carbon nanotubes, and ordered mesoporous carbon have also been extensively researched. When AC is compared to zeolites and MOFs, it is observed that AC is more hydrophobic, which makes them suitable for wet gas stream processes (Venkatesan, 2013).

There are three methods to activate the carbon mass to maximize its specific surface area: (i) physical activation by using CO₂/steam at high temperature (>800°C), which makes the process energy-intensive; (ii) chemical activation using strong acids (nitric acid – HNO₃, phosphoric acid – H₃PO₄), which act as the dehydrating agents in an inert atmosphere at relatively lower temperature (400-700°C), or bases (sodium hydroxide – NaOH, potassium hydroxide – KOH), or salts (potassium carbonate – K₂CO₃, zinc chloride – ZnCl₂, tin chloride – SnCl₂); and (iii) physio-chemical activation using combined techniques (Menya et al., 2018). With alkaline activation, the presence of the OH⁻ ions on the surface increases its efficiency to adsorb CO₂. Song et al. (2013) performed both types of activation experiments on corn cob and found that KOH chemical activation is better than steam activation when one is aiming for better CO₂ adsorption capacity.
CO$_2$ adsorption capacity is directly proportional to high specific surface area and presence of nitrogen-containing functional groups (Saxena et al., 2014).

After repeated cycles of adsorption and desorption, AC can be regenerated by thermal treatment and steam regeneration techniques. This step is necessary to address the issue of PSA operations for long-term. Bagreev et al. (2001) studied the impact of thermal treatment of used adsorbent at 300°C and found 100% regeneration of the adsorbents. Shah et al. (2013) reviewed the experimental and technical aspects of steam regeneration method and found that using steam increases the cost of the operation, and thus there is a need to study the steam impact on adsorbate reactivity.

### 2.3.2 Effects of activation parameters

The impregnation ratio (IPR), time of exposure for the activation and carbonization, and activation temperature are correlated factors. With the extreme increase in temperature and time, the overall mass yield decreases. Gratuito et al. (2008) chose response surface methodology to optimize the process to produce AC from coconut shell. They found that the optimal IPR of 1.725 (H$_3$PO$_4$: coconut shell), time of 19.5 minutes, and temperature of 416°C resulted in the formation of AC with an average pore diameter of 5 μm. For H$_3$PO$_4$ activation at a lower temperature, Yorgun and Yıldız (2015) concluded that increase in IPR increases the mesoporosity, but decreases the pyrolytic decomposition and specific surface area, whereas at higher temperatures better adsorbents are produced with higher pore volume. The presence of C=O functional groups (ketones, carboxyl, and lactone) in the AC disappears with an increase in temperature and IPR, which enhances the adsorbent properties. For KOH or NaOH activation, KOH activation occurs at a lower temperature (~400°C) when compared to NaOH (>570°C) (Basso et al., 2013). This
method is chosen to increase the aromaticity (C=C) index in the biochar as per the required adsorption characteristics. Moupong et al. (2015) characterized the KOH activated AC from tamarind seeds and confirmed the above using the Fourier-transform infrared spectroscopy (FTIR) analysis. It was also observed that carbon, oxygen, silicon, and potassium are the only elements detectable by energy dispersive spectrometer (EDS) on AC’s surface, and the carboxylic functional groups decreased with increase in temperature and use of KOH as the activating agent.

2.3.3 Raw materials for AC production

2.3.3.1 Coal

The most conventional raw material to produce carbon-based adsorbents is mineral coal. As per the ultimate and proximate analyses of different types of coal, the ones with maximum fixed carbon are used for the preparation of activated carbon. Teng et al. (2012) used Australian bituminous coal to produce AC via chemical activation using H$_3$PO$_4$ and further compared with physical activation using CO$_2$. They found that combined activation of the coal produced the best highly mesoporous AC with SSA as 687 m$^2$/g. The limitations of using AC derived from coal when compared to the wood-based ACs are high raw material costs, lower specific surface area, and unsuitable structure for the gas separation. This implies that not many studies are done to overcome these problems.

2.3.3.2 Biomass

An important current issue with the biomass industry is the generation of the massive amounts of rejects after the grinding and milling operations of biomass before any thermo-chemical conversion. This powdered biomass is found to have the potential to be turned into adsorbent
(activated carbon) after carbonization (Lozano-Castell et al., 2013). Since biomass has a high content of volatile matter, there is a need to decrease the hydrogen:carbon (H/C) ratio by carbonizing at high temperature and pressure as per Van Krevelen diagram (Álvarez-Gutiérrez et al., 2014). One of the processes to do so is by using hydro-thermal carbonization (HTC) within a temperature range of 180-300°C and pressures of 40-50 bar in the absence of O₂ with the specific biomass-to-solvent ratio. The hydrochar obtained is chemically or physically activated at high temperature (400-900°C) for a prolonged period (0.5-2 h), further breaking the complex bonds and increasing the porosity.

Pyrolysis is another process to decrease the H/C ratio of the biomass for improving characteristics of the biochar that will assist further activation. It is a form of carbonization of solid biomass in an inert environment of N₂ at 600-800°C. Recent studies on many food and agricultural wastes show that these are emerging sources to produce adsorbents with ultra-fine pores and higher SSA. It was found that these agricultural wastes upon exposure of different activation techniques can produce ACs of the specific surface area of about 250 - 2410 m²/g and pore volumes of 0.022 - 91.4 cm³/g. A few of them such as wheat, pinecone, rapeseed, pecan nut shells, rice straws, husks, and hulls, bagasse, eucalyptus, peach stones, grape seeds, and oat hulls were reviewed by Ioannidou and Zabaniotou (2007). They reviewed the pyrolysis reaction kinetics and segregated the study based on the isothermal and non-isothermal operation. As biomass constitutes a network of lignocellulosic compounds, it was difficult to define the order of the reaction. Hence, devolatilization reactions were categorized as first-order reactions. In Natalie Ho's thesis (Ho, 2012), the adsorbents were made by pyrolysis of anaerobic digestate by-product at a temperature in the range 500-700°C to maximize the pore size by breaking the lignocellulosic bonds. The most common raw material used for pyrolysis is coconut shell due to its sturdy structure.
Recent developments in the structural modification such as developing monolithic pores enhance the adsorption of CO\textsubscript{2} on the AC. Some non-carbon-based adsorbents such as calcium oxide (CaO), iron oxide (Fe\textsubscript{2}O\textsubscript{3}), zero-valent iron (Fe\textsuperscript{0}), iron chloride (FeCl\textsubscript{2}), silica gel, sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}), and alumina are also used to separate CO\textsubscript{2}, water vapor, siloxanes, and H\textsubscript{2}S from the raw biogas (Mamun and Torii, 2017). Table - 2.6 summarizes that the current progress of biomass-derived AC is driven by applications in gas separation, wastewater treatment, among others. Some of the commonly used adsorbents in numerous pre-treatment steps for the purification of biogas, such as H\textsubscript{2}S, H\textsubscript{2}O, and siloxanes removal, as well as in the CO\textsubscript{2}/CH\textsubscript{4} separation, are listed in Table - 2.7.
Table - 2. 6 Types of biomass and processes to prepare ACs and their uses

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Activation technique(s)</th>
<th>Adsorption study on</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cherrystones</td>
<td>Physical – Steam activated CO₂ activated</td>
<td>CO₂/CH₄ separation</td>
<td>(Álvarez-Gutiérrez et al., 2016)</td>
</tr>
<tr>
<td>Camphor leaves</td>
<td>HTC (180-300°C – 5 h) followed by KOH activation (800°C – 1 h)</td>
<td>CO₂ capture</td>
<td>(Guangzhi et al., 2017)</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>Both impregnated and un-impregnated KOH Pyrolysis (500°C – 1 h) or, HTC (300°C – 1 h) followed by inert activation (0.5-1 h)</td>
<td>Acetic acid</td>
<td>(West Virginia University, 2015)</td>
</tr>
<tr>
<td>Miscanthus x Giganteus straws</td>
<td>Pyrolysis (500-600°C – 70 min) followed by steam activation</td>
<td>N₂/77 K</td>
<td>(Michel et al., 2006)</td>
</tr>
<tr>
<td>Sunflower seed oil residue</td>
<td>Carbonization (700°C) followed by microwave assisted K₂CO₃ activation (2.45 GHz)</td>
<td>Methylene blue and acid 15 blue</td>
<td>(Foo and Hameed, 2011)</td>
</tr>
<tr>
<td>Cassava and Tapioca flour</td>
<td>HTC (250°C – 8 h) followed by KOH activation (800°C – 1 h)</td>
<td>N₂/77 K</td>
<td>(Pari et al., 2014)</td>
</tr>
<tr>
<td>Jatropha</td>
<td>Pyrolysis (400-600°C) followed by; KOH (evaporating 80°C – 24 h), H₃PO₄ (drying 60°C – 24 h) and, CO₂ activation (400°C – 30 min)</td>
<td>N₂/77 K</td>
<td>(Sricharoenchaikul et al., 2008)</td>
</tr>
<tr>
<td>Wood-based</td>
<td>Manufactured by Westvaco, H₃PO₄ activated</td>
<td>Wet H₂S gas stream</td>
<td>(Adib et al., 1999)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Carbonization followed by Physical or chemical activation</td>
<td>Liquid phase</td>
<td>(Suhas et al., 2016)</td>
</tr>
<tr>
<td>Olive residues</td>
<td>KOH impregnation followed by carbonization (300°C) followed by activation (840°C)</td>
<td>Supercapacitors electrodes</td>
<td>(Elmouwahidi et al., 2017)</td>
</tr>
<tr>
<td>Material</td>
<td>Treatment Process</td>
<td>Adsorbate</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------------------------------------------------</td>
<td>------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Cotton fibers</td>
<td>Carbonization (500°C – 0.5 h) followed by microwave induced H$_3$PO$_4$ activation</td>
<td>Methylene blue dye</td>
<td>(Duan et al., 2017)</td>
</tr>
<tr>
<td>Apricot shells</td>
<td>H$_3$PO$_4$ impregnation followed by carbonization (400°C – 1.5 h) and, dried (80°C – 24 h)</td>
<td>Tetracycline hydrochloride salt in aqueous solution</td>
<td>(Marzbali et al., 2016)</td>
</tr>
<tr>
<td>Pistachio nut shells</td>
<td>H$_3$PO$_4$ impregnation followed by carbonization (500°C – 2 h)</td>
<td>Methylene blue, rhodamine B, phenol, p-nitrophenol</td>
<td>(Attia et al., 2003)</td>
</tr>
<tr>
<td>Acorn shells</td>
<td>Different conc. of ZnCl$_2$ and HCl impregnation – 24 h each, followed by CO$_2$/H$_2$O physical activation (600°C – 30 min)</td>
<td>Iodine number</td>
<td>(Shahin and Saka, 2013)</td>
</tr>
<tr>
<td>Peanut hulls</td>
<td>Simultaneous activation and carbonization (600°C – 1 h) followed by iron nitrate impregnation</td>
<td>Methylene blue</td>
<td>(da Silva et al., 2017)</td>
</tr>
<tr>
<td>Date stones</td>
<td>Carbonization followed by physical, chemical or, physio-chemical activation</td>
<td>Phenols, dyes, pesticides, and heavy metals</td>
<td>(Ahmed, 2016)</td>
</tr>
<tr>
<td>Paulownia wood</td>
<td>H$_3$PO$_4$ impregnation (85°C – 6 h) then dried (110°C – 12 h) followed by activation (300-600°C – 1 h) and, dried (110°C – 12 h)</td>
<td>N$_2$/77 K</td>
<td>(Yorgun and Yıldız, 2015)</td>
</tr>
<tr>
<td>Tamarind seeds</td>
<td>Carbonization (500°C – 1 h) followed by KOH activation (500-700°C)</td>
<td>Iodine number, methylene blue, iron (III) from aqueous solution</td>
<td>(Mopoung et al., 2015)</td>
</tr>
<tr>
<td>Arundo dunax Linn &amp; Pomelo Peel</td>
<td>Impregnation in 85% H$_3$PO$_4$ (10 h) followed by activation (450°C – 1 h)</td>
<td>Ciprofloxacin hydrochloride</td>
<td>(Sun et al., 2016)</td>
</tr>
<tr>
<td>Material</td>
<td>Impregnation/Activation Procedure</td>
<td>Characterization Method(s)</td>
<td>Reference</td>
</tr>
<tr>
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<td>---------------------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>Reedy grass</td>
<td>60% H$_3$PO$_4$ impregnation (4 h) followed by activation (400-800°C – 1-4 h)</td>
<td>N$_2$/77 K, iodine number</td>
<td>(Xu et al., 2014)</td>
</tr>
<tr>
<td>Cocoa bean husk</td>
<td>Carbonization (1000°C – 0.5 h) followed by thermal treatments (215-900°C) CO$_2$ activation (880°C – 1-10 h)</td>
<td>N$_2$/77 K</td>
<td>(Plaza-Recobert et al., 2017)</td>
</tr>
<tr>
<td>Gulfweed</td>
<td>Carbonization (600°C – 0.5 h) KOH activation (350°C – 0.5 h; 700-850°C – 1.5-3 h)</td>
<td>N$_2$/77 K</td>
<td>(Li et al., 2017)</td>
</tr>
<tr>
<td>Waste tea</td>
<td>40% H$_3$PO$_4$ impregnation and activation (450°C – 1 h)</td>
<td>N$_2$/77 K K, methylene blue</td>
<td>(Kan et al., 2017)</td>
</tr>
<tr>
<td>Used tea (Camellia sinensis)</td>
<td>50% H$_3$PO$_4$ impregnation (24 h) followed by activation (200°C – 0.5 h; 400-800°C)</td>
<td>Iodine number, methylene blue</td>
<td>(Mahmood et al., 2017)</td>
</tr>
<tr>
<td>CCA (chromated copper arsenate) treated tree</td>
<td>Pyrolysis (700°C – 2 h) followed by H$_3$PO$_4$ impregnation, drying, and final activation (800-900°C – 1-4 h)</td>
<td>CO$_2$ capture</td>
<td>(Botom et al., 2017)</td>
</tr>
<tr>
<td>Plane tree seeds</td>
<td>Pyrolysis (850°C – 1 h) followed by CO$_2$ activation (650-850°C – 0.3-1 h)</td>
<td>n.a.</td>
<td>(Dodevski et al., 2017)</td>
</tr>
<tr>
<td><em>Glebionis coronaria</em></td>
<td>Pyrolysis (500-600°C – 2 h) followed by H$_3$PO$_4$ impregnation (1.5-2 h), drying (110°C – 24 h), and activation (400-500°C – 1-2 h)</td>
<td>Iodine number, methylene blue, heavy metals (cadmium, cobalt)</td>
<td>(Tounsadi et al., 2016)</td>
</tr>
</tbody>
</table>

n.a. – not available
Table - 2. 7 Types of universally used adsorbents for biogas upgrading process and their physical characteristics

<table>
<thead>
<tr>
<th>Different Adsorbents</th>
<th>Type of Adsorbent</th>
<th>Pore diameter (nm)</th>
<th>Pellet Density (kg/m$^3$)</th>
<th>Bulk density (kg/m$^3$)</th>
<th>Pellet Porosity</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Specific Surface area (m$^2$/g)</th>
<th>Adsorption Capacity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>Equilibrium</td>
<td>n.a.</td>
<td>984.3</td>
<td>670.6</td>
<td>0.506</td>
<td>n.a.</td>
<td>845.87</td>
<td>0.25 mmol/s</td>
<td>(Shen et al., 2011)</td>
</tr>
<tr>
<td>Activated Biochar after HTC</td>
<td>Kinetic</td>
<td>0.8-2.0 &lt;2.0</td>
<td>n.a.</td>
<td>390-430 n.a.</td>
<td>n.a.</td>
<td>1.15-1.35 0.62-0.97</td>
<td>2250-2850 1260-1940</td>
<td>2.9-3.5 CO$_2$ mmol/g 3.9-4.8 CO$_2$ mmol/g</td>
<td>(Lozano-Castell et al., 2013) (Sevilla et al., 2013)</td>
</tr>
<tr>
<td>Alkaline Activated Biochar</td>
<td>Kinetic</td>
<td>2.35-2.84</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>&gt;2</td>
<td>514.98-1633.71</td>
<td>0.12-0.80 CO$_2$ mmol/g</td>
<td>(Guangzhi et al., 2017)</td>
</tr>
<tr>
<td>Monolithic Activated Carbon</td>
<td>Kinetic</td>
<td>5000-15000</td>
<td>1086-1364</td>
<td>550-710</td>
<td>n.a.</td>
<td>0.469-1.047</td>
<td>2200</td>
<td>6.71-10.18 CH$_4$ mmol/g</td>
<td>(Machnikowski et al., 2010; Sato et al., 2014; Rezaei and Webley, 2010)</td>
</tr>
<tr>
<td>Carbon Molecular Sieve 3K</td>
<td>Kinetic</td>
<td>0.4-0.9</td>
<td>1060</td>
<td>715.43-750</td>
<td>0.46</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~98% CO$_2$ capture</td>
<td>(Grande, 2011; Grande et al., 2008)</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>Equilibrium</td>
<td>0.5-1</td>
<td>1324</td>
<td>645-660</td>
<td>0.338</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~98% CO$_2$ capture</td>
<td>(Agarwal, 2010; da Silva Santos et al., 2011)</td>
</tr>
<tr>
<td>Zeolite 5A</td>
<td>Kinetic</td>
<td>0.5-1</td>
<td>1160</td>
<td>n.a.</td>
<td>0.64</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~99% CO$_2$ capture</td>
<td>(Augelletti et al., 2017)</td>
</tr>
<tr>
<td>Activated Carbon from Pyrolysis</td>
<td>Kinetic</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.05-0.22</td>
<td>62.1-317.6</td>
<td>24.22 mg/g H$_2$S</td>
<td>24.22 mg/g H$_2$S</td>
<td>(Ho, 2012)</td>
</tr>
<tr>
<td>MOFs</td>
<td>n.a.</td>
<td>0.85-1.36</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~2000</td>
<td>0.5-8 CO$_2$ at 4 MPa</td>
<td>(Llewellyn et al., 2009)</td>
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<td></td>
<td></td>
<td>1.18-14.6 H₂S (Hamon et al., 2009)</td>
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<tr>
<td>n.a. – not available</td>
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</table>
2.4 References


3 SYNTHESIS OF THE HYDROCHAR AND BIO- ADSORBENT FROM SWITCHGRASS

3.1 Introduction

The production of low-cost mesoporous and nanoporous adsorbents from bio-waste has increased with the development of carbonization technologies such as wet torrefaction or hydrothermal carbonization (HTC) of agricultural and forest waste. Recently developed two-step novel approach to obtain such bio-adsorbents with a high specific surface area (> 600 m²/g) comprises of subsequent hydrothermal treatment of biomass and physical or chemical activation (Álvarez-Gutiérrez et al., 2014).

HTC is a technology to increase the carbon content of biomass to form hydrochar by decreasing O/C and H/C ratio at a lower temperature range at the expense of high pressure. The operating range for this process is 180-300°C in an inert atmosphere (mostly N₂), at 20-60 bar (Basso et al., 2013). Kim, Yoshikawa, and Park (2015) studied the characteristics of biochar obtained after HTC (150-280°C) of cellulose. They concluded that the biochar obtained after HTC beyond 220°C showed decomposition of cellulose by undergoing decarboxylation reaction that owed to an increase in aromatic and aliphatic carbon regimes. Jain et al. (2016) reviewed the hydrothermal means to produce ACs. They specified that the presence of a large number of oxygenated functional groups (OFGs) on the hydrochar is the ultimately favorable characteristic that contributes to high porosity in the ACs. It is due to the presence of phenolic compounds after hydrothermal conversion of the lignin in the biomass. HTC is a pretreatment method necessary for the biomass to remove the volatile matter and enhance the carbon content, as the lignocellulosic bonds break. The presence of OFGs, phenolic, aromatic, aliphatic compounds, assists the following activation step to form micropores of pore diameter less than 1 nm (Nizamuddin et al.,
It is found to be most favorable to increase CO₂ adsorption since the molecular size of CO₂ is 0.232 nm (Calvo-Muñoz et al., 2016). Also, the presence of nitrogen-containing compounds (NCC) increases CO₂ capture (Huang et al., 2017). Addition of catalysts such as acrylic acid, acetic acid supports the dehydration reaction, however, alkali boosts the decarboxylation reaction. However, alkali, when used at high temperature, enhances the hydrothermal liquefaction to form biofuels (Toor et al., 2011). Metal oxides-based catalysts are also known to increase the nitrogen-containing aliphatic compounds of the biomass by decarboxylation which is a desirable property for CO₂ and H₂S adsorption (Liu et al., 2018). Alkali pretreatment of lignin-rich biomass helps in delignification, dissolution of hemicellulose, saponification of intermolecular ester bonds (Kim et al., 2016). Mostly used chemical activators are phosphoric acid (H₃PO₄), potassium hydroxide (KOH), tin chloride (SnCl₂), zinc chloride (ZnCl₂), potassium carbonate (K₂CO₃) which reacts at temperatures higher than 400°C. The physical activators are CO₂ and steam which activates the adsorbent at high pressure and temperature (Shahin and Saka, 2013). Deng et al. (2010) studied microwave assisted KOH and K₂CO₃ activation of the cotton stalk. It was found that KOH activation contributed to high micropore volume when compared to the K₂CO₃ activation process. Nowruouzi et al. (2017) developed a counter-current approach by recycling KOH solutions to derive AC from waste tissue papers with a high specific surface area 1820 m²/g. These studied reveals that KOH is the most suitable activator for various carbon-based materials to produce ACs with excellent adsorptive features.

Switchgrass (Panicum virgatum) is a North American perennial grass which has been contributing to the biomass industry in the form of second-generation energy crop since the 1980s. It generally comprises of 40.43% cellulose, 31.55% hemicellulose, 9.98% lignin, and 12.57% extractives (Monti, 2012). Regmi et al. (2012) used switchgrass to produce adsorbents for cadmium and
copper removal using cold activation technique by impregnation the biochar in various concentrations (conc.) of KOH. However, the Brunauer-Emmett-Teller (BET) analysis results for the total surface area was only 5.01 m$^2$/g which is very low when compared to commercial activated carbon for gas separation purposes.

In this study, switchgrass is exposed to HTC with and without alkaline solvent and was further subjected to mild chemical activation. Since KOH reacts with carbon at temperatures above 450°C (Basso et al., 2013) some amount of unreacted KOH remains stuck in the hydrochar along with the inorganic salts obtained after neutralization reaction during the HTC. These salts depositions contributed to heighten the tortuosity of bio-adsorbents in the chemical activation step. The objective is to compare alkaline HTC derived AC, and de-ionized HTC derived AC production process. The parameters considered in this research are moderate hydrothermal pretreatment temperature, low retention time, and solvent pH during the HTC. Furthermore, the activation temperature was fixed at 700°C (±3°C) to study the nature of the bio-adsorbents produced from the de-ionized water-based hydrochar (DH) and alkali-based hydrochar (KH). Use of KOH during HTC improved the bio-adsorbent properties, precisely the specific surface area to 339.98 m$^2$/g (post chemical activation).

### 3.2 Material and Methods

The switchgrass fines (SF) were obtained after milling and grinding operations for bio-energy production from Nott farms, Clinton, Ontario, Canada. The SFs were used as received as the raw material to produce the ACs. It was sieved to know the particle size distribution in the sieve shaker (50-710 μm). Potassium hydroxide (KOH) of certified ACS grade (≥ 85.0%, Fischer-Scientific) was used. De-ionized (DI) water was used for the comparison of HTC performance (pH -
5.92±0.13) against KOH as an alkali catalyst (pH – 10±0.13) to achieve maximum OFGs and NCCs on hydrochar.

### 3.2.1 Mode of operation of HTC

The HTC experimental procedure was followed to comply with the safety protocol. Considering the moisture content in the SFs, a 1:12 ratio of SFs: solvent was used as the feedstock for the hydrothermal carbonization. The HTC experiments were performed in a stainless steel 1 L Parr reactor with a glass lining at 200°C and 240°C (±5°C). These temperatures were selected based on the thermal degradation of the raw SFs in the TGA experiments. The reactor was pressurized initially with N₂, but, with an increase in the temperature the pressure autogenously increased up to 60±0.06 bar. The holding time was fixed for 30 and 60 min to obtain desirable hydrochar since prolonged exposure time is found to lower the mass yield as well as effects on the H/C and O/C ratios is negligible (Jain et al., 2016).

Figure 3. 1 HTC experimental setup to produce hydrochar and alkaline-based hydrochar
The alkali-based hydrochar with KOH (are denoted by KH) and spent solvent were obtained after the reactor cooled down and depressurized to atmospheric pressure. The products were filtered and dried at 105±2°C for 24 h in the muffle furnace. The alkali-based hydrochar were named as KH200-30, KH200-60, KH240-30, and KH240-60. The other type of hydrochar were prepared (are denoted by DH) using the similar conditions in the reactor where 250 ml of DI water was added with 25 g of SFs. The following acquired products were named DH200-30, DH200-60, DH240-30, and DH240-60. All the products were stored separately in sealed plastic bags. The pH 10 (±0.13) was considered after analyzing the effects of pH on the biomass at a fixed temperature since high pH resulted in biomass conversion to tar.

3.2.2 Synthesis of bio-adsorbent

The proximate analysis was carried out in a muffle furnace as per ASTM standards to know the volatile matter (VM), ash (A), and fixed carbon (FC) content. 10 g of each of the samples was dried at 105±2°C for 24 h. The dried samples were placed in a desiccator with silica gel as the desiccant to avoid moisture absorption onto the sample during the cooling process. The dried sample was reweighed to calculate moisture content (ASTM-E871). The dried sample was stored in a sealed bag for other analysis. 0.5±0.006 g of the dried sample was heated at 575±3°C for 5 h, followed by cooling down to 105±2°C in the furnace and further to ambient temperature in the desiccator. The difference in the initial and final weight predicted the ash content (ASTM-E1755). For the calculation of volatile matter content, 0.5±0.006 g of the dried sample was ignited at 950°C for 7 min followed by cooling to room temperature in the desiccator. The difference in weight estimated the volatile matter (ASTM- E872). The equation 3.1 was used to determine the amount of fixed carbon after measuring the volatile matter, ash content, and moisture.
FC = Total dried weight of the selected sample – A – VM  

The dried SFs and different type of hydrochar were subjected to elemental/ultimate analysis to determine composition based on the weight percentage of carbon, hydrogen, nitrogen, oxygen, and sulfur using CHNS analyzer (FLASH 2000 Series, Thermo-SCIENTIFIC). The mass degradation with an increase in temperature was determined in the DSC-micro TGA (Q600, TA Instruments, USA) analysis was run at a heating ramp rate of 10°C/min and under an N₂ flow of 5 ml/min. The samples were placed in an alumina crucible and heated to 1000°C followed by rapid cooling. The OFGs and NCCs qualitative assessment were examined in FT-IR (FTIR Spectrometer UATR Two, Perkin-Elmer) with diamond crystal ATR. The samples were placed on a clean sample holder platform and examined at 75±3 MPa screwing pressure.

The hydrochar which were found to have maximum OFGs and NCCs were selected as the feedstock to activate. They were activated in a stainless-steel tube reactor (Fig.3.2.) at 700±3°C under an N₂ atmosphere at a flow rate of 100 ml/min for 1 h. The reactor was cooled to atmospheric temperature with the reduced N₂ flow. The bio-adsorbent were named as, DHAC700 and KHAC700. The ACs were washed several times using DI water until the pH got neutral followed by drying at 105±2°C for 24 h and was stored in a desiccator before the surface characterization and other studies.

The chemical activation requires KOH dosage so that the hydrochar reacts with the alkali and breaks lignin. This step supports the bio-adsorbent to be more microporous in nature since the KOH reacts with the carbon (present in the form of volatile matter) and open a network of pores. This interconnected pores and the channels promotes the tortuosity of the bio-adsorbent formed. The bio-adsorbent formed after the chemical activation consists of some amount of K₂CO₃ on the
surface. Chemical activation is a series of redox reactions occurring in the absence of oxygen at different temperatures to attain graphene state for the feedstock. The primary goal is to create pores by breaking the aromatic bonds of the lignin as it removes the oxygen-containing and nitrogen-containing compounds. The oxides are released, and that makes a vacant space on the solid adsorbent surface. This study was performed at a maximum temperature of 700°C. The dehydration of KOH started at 400°C. Hence, there is the production of K₂CO₃ at the same temperature followed by complete usage of KOH at 600°C. The reactions are as follows:

\[ 2\text{KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \]  
\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  
\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  
\[ \text{CO}_2 + \text{K}_2\text{O} \rightarrow \text{K}_2\text{CO}_3 \]

But if there is an increase in the temperature (~800°C), K₂CO₃ could degrade into metallic potassium and CO. The reactions are as follows:

\[ \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2 \]  
\[ \text{CO}_2 + \text{C} \rightarrow 2\text{CO} \]  
\[ \text{K}_2\text{CO}_3 + 2\text{C} \rightarrow 2\text{K} + 3\text{CO} \]  
\[ \text{C} + \text{K}_2\text{O} \rightarrow 2\text{K} + \text{CO} \]  
\[ 6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \]
This could lead to incorporation of the metallic K into the bio-adsorbent. To assure the complete cleansing of the bio-adsorbents, they were washed thoroughly several times using DI water until the filtrate achieved pH 7.

![Experimental Setup](image)

Figure 3.2 Experimental Setup for activation of the hydrochar to produce the bio-adsorbents

### 3.2.3 Morphological Characterization

The ACs were also characterized using the Brunauer-Emmett-Teller (BET) analyzer (Quantachrome Autosorb-iQ, ATS Scientific Inc.) using N\textsubscript{2} adsorption isotherm at the temperature of 77 K. The ACs were outgassed at 300°C for 5 h. The total pore volume and total specific surface
area were measured at relative pressures of 0.01-1.0. The pressure range was chosen as 0.05-0.25 for estimation of specific surface area and 0.995 for pore volume prediction. The curve in the test relates the adsorption of adsorbate (liquid N\textsubscript{2}) with respect to each pressure value. Thus, the proportionality constant C aids in the determination of the BET surface area. To evaluate the mesopore volume, the point is considered when the curve finally drifts from the progressive linear pattern. The mesopore surface area is calculated as (Galarneau et al., 2014):

\[ \text{Mesoporous surface area} + \text{External specific surface area} = \text{Total specific surface area} \quad (3.2) \]

The microstructures and structural morphology were observed using scanning electron microscope (SEM) (Quanta FEG – 250, FEI) after sputtering the samples with gold under high vacuum (Denton Vacuum at ~9e-5 Torr) to improve the conductivity. The magnifying range was chosen up to 96,000x with a high vacuum accelerating voltage of 10.00 kV, probe current (< 200 nA), and a working distance of 8.9 mm.
3.3 Results and Discussions

3.3.1 Physical and Chemical properties of switchgrass fines

The FT-IR analysis of SF indicates several peaks confirming the presence of multiple functional groups and elements. The primary component of any kind of biomass is carbon-based. Hence, the functional groups associated are organic molecules. Thus, the wavelength range for this analysis is chosen from 400-4000 cm\(^{-1}\). Aliphatic hydrocarbons (–C-H), aromatic compounds (–C=C), OCCs (alcohols and phenols –C-OH, ethers –C-O-C, aldehydes –C=OH, ketones –C=O, esters –C=OO-C, carboxylic acids –COOH and anhydrides –C=O-O-C=O), nitrogen-containing compounds (amines –N-H and amides –ONH), halogen-containing compounds, heterocyclic compounds, boron compounds, silicon compounds, phosphorus compounds, and sulfur compounds are detectable in this range. Table 3.1 lists the functional groups detected by FT-IR analysis. The maximum vibrations generated during the analysis of SF are due to the aliphatic stretching, OCCs-stretching, phosphorus and silicon stretching, and NCCs-bending.
Table 3.1 Functional groups detected by the FT-IR analysis for all the samples

<table>
<thead>
<tr>
<th>Characteristic of the peak</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sharp peak at 1100 cm(^{-1})</td>
<td>Si-O-Si asymmetric stretching</td>
</tr>
<tr>
<td>Dual peaks ~1500-1700 cm(^{-1})</td>
<td>Bending of primary, secondary and tertiary amides</td>
</tr>
<tr>
<td>Broad mount ~3000-3600 cm(^{-1})</td>
<td>–C-OH and –C-H stretching</td>
</tr>
<tr>
<td>Numerous peaks ~1200-1350 cm(^{-1})</td>
<td>Aromatic and aliphatic amines twisting and wagging</td>
</tr>
<tr>
<td>Minor peaks ~400-800 cm(^{-1})</td>
<td>Presence of halogen-containing compounds (–C-X)</td>
</tr>
<tr>
<td>Broad bands ~650-1300 cm(^{-1})</td>
<td>1. Phosphorus-containing esters, phosphine wagging</td>
</tr>
<tr>
<td></td>
<td>2. Aliphatic stretching (in-plane ~650 cm(^{-1}) and out-plane ~1275 cm(^{-1}))</td>
</tr>
</tbody>
</table>

The mass yield was calculated in Table 3.2 for different hydrochar, and bio-adsorbents were calculated based on the mass of the dry raw SFs (Eqn. 3.3). Since some of the processes consisted of the addition of KOH, the mass was added to the dried SF and hydrochar too for before the procedure (Eqn. 3.4).

\[
\text{Mass yield (\%)} = \frac{\text{Mass of dried hydrochar or bio-adsorbent}}{\text{Mass of dried SF (before HTC)}} \times 100 \% (3.3)
\]

\[
\text{Mass yield \ast (\%)} = \frac{\text{Mass of dried hydrochar or bio-adsorbent}}{\text{Mass of dried SF + (Mass of KOH added before HTC)}} \times 100 \% (3.4)
\]

The carbon content improved upon hydrothermal pre-treatment with DI water. This was due to the initiation of the carbonization due to increase in temperature and autogenously developing pressure. The significant decrease in O/C ratio (1.046 to 0.554) and H/C ratio (0.127 to 0.105) confirms that there is the breaking of the hemicellulose occurring at 200°C up to 240°C. The second set of experiments for time showed a decrease in the mass yield at the same temperature, that confirms that the change in the composition is dependent on both the parameters. The addition of KOH to the hydrothermal pre-treatment increased the ash content; however, it accelerated the carbonization process giving rise to the products with higher carbon content. The O/C and H/C
ratio for the DHs and KHS decreased by 17.87% and 23.8% which proves that KHS are better-carbonized products.
Table - 3.2 Characterization of SF, DHs, KHs, and bio-adsorbents

<table>
<thead>
<tr>
<th>Sample id</th>
<th>Ultimate analysis (%)</th>
<th>Proximate analysis (%)</th>
<th>Mass Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>SF</td>
<td>44.21±1.03</td>
<td>5.63±0.20</td>
<td>0.77±0.09</td>
</tr>
<tr>
<td>DH200-30</td>
<td>52.70±0.86</td>
<td>5.64±0.91</td>
<td>0.69±0.06</td>
</tr>
<tr>
<td>DH200-60</td>
<td>53.43±1.21</td>
<td>5.43±0.38</td>
<td>0.91±0.15</td>
</tr>
<tr>
<td>DH240-30</td>
<td>54.01±1.42</td>
<td>5.56±0.64</td>
<td>0.91±0.08</td>
</tr>
<tr>
<td>DH240-60</td>
<td>58.96±1.70</td>
<td>6.24±0.35</td>
<td>1.01±0.12</td>
</tr>
<tr>
<td>KH200-30</td>
<td>53.58±2.03</td>
<td>5.64±0.61</td>
<td>0.68±0.81</td>
</tr>
<tr>
<td>KH200-60</td>
<td>55.97±0.61</td>
<td>5.56±0.23</td>
<td>0.86±0.12</td>
</tr>
<tr>
<td>KH240-30</td>
<td>59.86±1.49</td>
<td>5.81±0.05</td>
<td>1.45±0.07</td>
</tr>
<tr>
<td>KH240-60</td>
<td>62.24±1.82</td>
<td>5.01±0.90</td>
<td>1.49±0.11</td>
</tr>
<tr>
<td>KHAC700</td>
<td>86.34±0.76</td>
<td>2.23±0.48</td>
<td>3.45±0.05</td>
</tr>
<tr>
<td>DHAC700</td>
<td>84.13±1.07</td>
<td>2.61±0.15</td>
<td>3.48±0.75</td>
</tr>
</tbody>
</table>
The PSD (Fig.3.4) is the particle size analysis of the switchgrass fines obtained from the Nott Farms. The sample procured showed that the maximum amount of the fines are sized as 250 µm and 710 µm. Thus, it was suitable to produce bio-adsorbent of the size of granular characteristics instead of powdered properties.

![PARTICLE SIZE DISTRIBUTION CURVE](image)

*Figure 3.4 PSD curve of raw switchgrass fines obtained from the Nott Farms*

### 3.3.2 Formation of the ACs

Firstly, during the alkali hydrothermal pretreatment, the lignocellulosic bonds of the biomass breaks to expose the OFGs and NCCs. The acid released during this process forms potassium salts, and both the unreacted KOH and salts impregnate uniformly into the hydrochar. Furthermore,
thermal activation at both the temperatures developed numerous homogeneously distributed mesopores and micropores with pore size ~ 0.4-1.07 nm.

### 3.3.3 Physical and Chemical properties of DHs, KHs, and ACs

The remaining solvent pH obtained after de-ionized water-based HTC and alkaline-based HTC after 30 and 60 minutes at 200°C and 240°C results are presented in the Fig. 3.5. It was observed that pH decreased with increase in time of reaction due to the gradual release of carboxylic acids. The pH of the alkali solvent after HTC was further lower when compared to the pH of the de-ionized water after HTC due to the catalyzed reactions occurring during the HTC. However, the mass yield decreased with increasing temperature due to the conversion of the SFs to bio-oil. The break-down of Si-O bonds and reaction of K during the HTC goes to the residual solvent that has contributed to the higher pH value for the alkaline-based HTC treatment. The KH-hydrochar was found to have higher ash content when compared to the DH-hydrochar due to deposition of Si-salts and K-salts formed during the reaction as well as unreacted KOH stuck onto the dried hydrochar.

<table>
<thead>
<tr>
<th></th>
<th>Initial pH</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH200-30</td>
<td>5.92</td>
<td>2.93</td>
</tr>
<tr>
<td>DH200-60</td>
<td>5.92</td>
<td>2.89</td>
</tr>
<tr>
<td>DH240-30</td>
<td>5.92</td>
<td>2.71</td>
</tr>
<tr>
<td>DH240-60</td>
<td>5.92</td>
<td>2.67</td>
</tr>
<tr>
<td>KH200-30</td>
<td>10</td>
<td>3.18</td>
</tr>
<tr>
<td>KH200-60</td>
<td>10</td>
<td>3.1</td>
</tr>
<tr>
<td>KH240-30</td>
<td>10</td>
<td>2.87</td>
</tr>
<tr>
<td>KH240-60</td>
<td>10</td>
<td>2.84</td>
</tr>
</tbody>
</table>

**Figure 3.5 pH of the remaining solvent before and after the different hydrothermal treatments**
Fig. 3.6 represents the TGA curve of the SF, DHs, and KHS, and ACs. Since dry samples were chosen for the study, initial weight loss could be attributed to the interstitial equilibrium moisture loss till 200°C. The SF’s TGA curve explains the decomposition (carbonization) starts at 240 °C. This stands right with the beginning of thermal degradation of hemicellulose (Yang et al., 2007). Hence, 200° and 240°C were chosen as the standard test temperature for the comparison of both types of hydrothermal pre-treatment as it would assist the exposure of the OFGs. At 375°C, another drop in the weight percentage was recorded. This marks the initiation of cellulose breakdown at a higher temperature. Since increasing the temperature decreases the presence of OFGs (Jain et al., 2016), thus, at 600°C, the SF loses its maximum volatile compounds and undergoes a delignification process followed by the extractives decomposition. For KH24030 and DH24030, the weight loss increased rapidly till 500°C, and the activation appeared around 700°C since the
weight significantly reduced due to the elimination of the maximum volatile functional groups. The removal of aromatic compounds and polyphenolic groups from the grass lignin in the hydrochar results in an increase of microporosity and mesoporosity in the bio-adsorbents. The curves of both bio-adsorbents were compared, and it was observed that the stability of the curve was higher in KHAC700 since the devolatilization was catalyzed by the alkaline pre-treatment of the feedstock after activation that induced better delignification.

![Comparison of FTIR analysis of DHs](image)

**Figure 3. 7 FTIR analysis of DI water-based hydrochar**

The Fourier spectrum for the DI water-based hydrochar followed the similar pattern like of the raw SF. There were slight changes observed after varying temperature and time due to the –C-H stretching. At 240°C, it can be significantly noticed that the curve became flat at 1100 cm\(^{-1}\) since the silicon compounds in the raw SF started to break down with increasing temperature and time exposing the oxygen bonds. It not only contributed to the OCCs but also to the exposure to the
NCCs. The rise of the graph at 1600 cm\(^{-1}\) for both the temperatures confirms the above stated as the amines bending released hydrogen from the NCCs. For DH24030 and DH24060 the difference was observed at broad mount peak after 3000 cm\(^{-1}\). This proves prolonged hydrothermal treatment breaks the carboxylic chains and the number of oxygen decreases. This was the reason for choosing DH24030 for the following activation step.

![FTIR: KHz](image)

**Figure 3. 8 FT-IR analysis of the alkaline-based hydrochar**

The curve for KH20030 was similar to the raw SF’s analysis, with changes for the aliphatic bonds. However, the analysis for the KH24030 sample showed substantial improvement for the dual peaks indicating higher bending and twisting the primary, secondary, and tertiary amines. The OCCs mounts after 3000 cm\(^{-1}\) were observed to be highest for the KH24030 sample. Since the abundant presence of these compounds contributes to the better activation. Thus, KH24030 was chosen to compare the activation to the DH24030.
The curve for both bio-adsorbents was similar. However, the NCCs were found to have a higher absorbance in the KHAC700. The flatter graphs of both the bio-adsorbents analysis suggest that the hydrochar have undergone a high level of aromatization during the chemical activation that has opened its microporous structure. The difference between the curves appears for the dips at 1250, 1750, and 300 cm\(^{-1}\) in DHAC700. The trend follows the same pattern of the absorbance for the Si-O bonds. The phenolic stretching has decreased which suggests high delignification. The smooth slope at 3000 cm\(^{-1}\) indicates elimination of the volatile compounds mostly alcoholic, carboxylic, and others in nature. Since hydrothermal pre-treatment and the activation were performed in a controlled environment (no O\(_2\)), the carbon stayed on the surface releasing the OH-bonds in the form of water vapor and creating micropores.
3.3.4 Surface and adsorptive characteristics of ACs

Fig. 3.10. shows a remarkable change in structural morphology using a different range of magnification in SEM for different specimens. The uniformly connected porous network and tortuous nature of the ACs were detected. The hydrochar had a minimum porous structure with abundance crystals of untreated KOH and organic salts depositions. The SFs resembled long fibers with large porous skeletal structure. The SEM images of the ACs at a scale of 300 nm (Fig. 3.10. (e), (f)) denotes the superior imaging of the micropores which has high potential to contribute towards excellent selective adsorption of CO₂ based on the difference of the pore size.
Figure 3. 10 (a) Surface of Raw SFs at 200x (b) Surface of raw SF at 1,000x (c) Surface of KOH24030 at 10,500x (d) Surface of DH24030 at 7000x (e) Surface of KHAC700 at 96,000x (f) Surface of DHAC700 at 95,000x

Figure 3. 11 BET: Linear isotherm curve for KHAC700

De Lange et al. (2014) have explained the calculation of the specific surface area from the curve. The relative pressure data points (p/p₀) considered for the calculation are less than unity. Since
multilayer adsorption starts to occur when the pressure increases, IUPAC suggested that the slope is calculated for the data points (0.05,0.3). If the scale is increased, then the values deduced from the curve (intercept I, slope s, and constant C) will give a negative value that does not denote anything. To formulate the BET equation and BET linearized equation there are three assumptions.

1. The adsorbent has a homogenous surface where adsorbate molecules are clinging in a multilayer manner which is not similar to the Langmuir’s theory.

2. For multilayer adsorption, the adsorbate molecules can accumulate on the first layer even if the pores are not filled.

3. The molar adsorption energy is constant for each layer as there are no lateral interactions between the adsorbate molecules in one layer.

The following equations are used to measure the values to give specific surface area:

\[ q_b = q_{bm} \left( \frac{C \left( \frac{P}{P_o} \right)}{\{1 - \left( \frac{P}{P_o} \right) + C \left( \frac{P}{P_o} \right)\} \cdot \{1 - \left( \frac{P}{P_o} \right)\}} \right) \]  \hspace{1cm} (3.5)

\[ C \sim e^{\left( \frac{E_1 - E_2}{RT} \right)} \]  \hspace{1cm} (3.6)

\[ S_b = \frac{q_{bm}\rho_{STP}N_AN_{2}}{M_{N_2}} \]  \hspace{1cm} (3.7)

\[ q_b \left( \frac{P}{P_o} \right) = \left( \frac{1}{Cq_{bm}} \right) + \left( \frac{C - 1}{Cq_{bm}} \right) \cdot \left( \frac{P}{P_o} \right) = I + s \left( \frac{P}{P_o} \right) \]  \hspace{1cm} (3.8)

\[ q_{bm} = \left( \frac{1}{I + s} \right), C = \left( \frac{I + s}{I} \right) \]  \hspace{1cm} (3.9)
Where, \( q_b \) is BET multilayer adsorption capacity, \( q_{bm} \) is BET monolayer adsorption capacity, \( C \) is dimensionless constant for BET, \( E_1 \) and \( E_2 \) are molar adsorption energy for the first layer and further layers respectively, \( \rho_{v, STP} \) is the density of nitrogen (N\(_2\)) vapor at standard temperature and pressure (STP), \( N_A \) is Avogadro’s number \((6.022 \times 10^{23})\), \( M_{N2} \) is the molecular mass of N\(_2\), and cross-section of N\(_2\) molecule \((0.162 \, \text{nm}^2)\).

The slope, intercept, and constant can be evaluated using two data points in the range of \((0.05,0.30)\) using the following equation.

\[
\begin{align*}
    s_{i+1} &= \frac{y_{i+1} - y_i}{x_{i+1} - x_i}, \\
    I_{i+1} &= y_i - x_i s_{i+1}, \\
    C_i &= \frac{I_i + s_i}{I_i} \\
\end{align*}
\]

The uncertainty analysis can be formulated using the variance equation accounting independent random errors. Confidence intervals are used in the error analysis for measured temperature \((\pm 0.1 \, \text{K})\), relative pressure range \((\pm 0.1\%)\), volume \((\pm 5\%)\), and weight of the sample \((\pm 0.1 \, \text{mg})\). The uncertainty arises during the determination of the pore volume and BET surface area. However, for microporous adsorbent the uncertainty increases due to significant N\(_2\) adsorption even at relative low-pressure points which are not considered to evaluate the slope, intercept, and constant. The exact amount of adsorbed N\(_2\) is higher than the general amount. Thus, this process is not used to determine the pore volume uncertainty.

\[
V_p = \frac{q_{sat} \rho_{v, STP}}{\rho_{NBP}}
\]

Where \( V_p \) is pore volume, \( q_{sat} \) is loading at saturation ml/g, \( \rho_{NBP} \) is the density of liquid N\(_2\) at a normal boiling temperature (NBT).
Another parameter considered for the BET surface area uncertainty is the number of degrees of freedom (F). IUPAC has specified to evaluate the slope, intercept, and constant by using at least five data points, i.e., F = 3 to reduce the uncertainty. For this study, in the Quantachrome apparatus, the values were determined after averaging three tests, and the data fitting was done to the curve of the multi-point BET equation in the machine itself. It generated the values with a correlation coefficient (r) of 0.97 as BET summary of \( s = 13.486 \text{ g}^{-1} \), \( I = -3.241 \text{ g}^{-1} \), and \( C = -3.161 \). The negative value of C denotes that the ASiQwin™ software used the upper limit of the p/p\(_0\) as \( \leq 0.35 \). This might be one of the reasons that the results did not align to the linearized equation and resulted in the lower surface area. The data-points could have been considered as p/p\(_0\) \( \leq (0.01,0.10) \) to identify the trend of microporous adsorption capacity to reach up to \( \sim 230 \text{ cm}^3/\text{g} \).

For the pore diameter calculations, the equations used to find the diameter of the slit-like micropores (\( r_K \)) and cylindrical pore (\( r_p \)) are:

\[
r_K = \frac{2V_m\sigma\cos(\alpha)}{RT\ln\left(\frac{p}{p_0}\right)}
\]

(3.12)

\[
t = \left(\frac{-0.1399}{\ln\left(\frac{p}{p_0}\right)} - 0.034\right)^{0.5} \text{ (assuming the thickness < 1 nm)}
\]

(3.13)

\[
r_p = r_c + th
\]

(3.14)

Where, \( r_K \) is Kelvin radius for slit pore (nm), \( V_m \) is molar gas volume of N\(_2\) (34.68 cm\(^3\)/mol), \( \alpha \) is contact angle (0°), \( \sigma \) is the surface tension of N\(_2\) (8.72 x 10\(^{-3}\) N/m), and \( th \) is the
thick of the film (nm). The slit shape microporous radius varies from 0.41 to 0.78 (±0.005) nm, and the cylindrical pores vary from 0.57 to 1.07 (±0.001) nm since $p/p_o$ is (0.10,0.30).

The graph showed the relationship of adsorbed total nitrogen volume in cm$^3$ per mass of the sample studied (g) versus the relative pressure points ($p/p_o$) from 0.10 to 0.90. The total volume in the higher $p/p_o$ range concludes that the adsorption isotherm curve was for mesoporous surfaces which slightly contributed to the increase in volume adsorbed. The linear BET isotherm for the bio-adsorbent KHAC700 shows that the specific surface area was 339.92 m$^2$/g as per the interpolated software results. It was calculated to be 422.39 m$^2$/g. Thus, the error percentage could be due to insignificant negative BET constant. The lower surface area is due to the insufficient KOH:hydrochar ratio. Moreover, the minimum pore size was found to be very narrow at 0.41-1.07 nm. The extensively small pore size is due to the additional heating of the salts deposited on the hydrochar during the activation. It was predicted by the isotherm curve (category 1) which represents that most of the pores were microporous in nature (Vishnyakov et al., 1999). The process took a long time that adds to the fact of slow diffusion due to the small pore size. The pore volume at STP was found to be 0.402 cm$^3$/g. This proves that the hydrothermal pre-treatment enhanced the distribution of the -COOK group throughout the biomass. The reaction of KOH with the -COOH group during hydrothermal pre-treatment reduced the OCCs and attributed the increase in mesoporous surface area.

3.4 References


4 EXPERIMENTAL FIXED BED ADSORPTION OF CO$_2$ ON BIO-ADSORBENTS

4.1 Introduction

The carbon capture, utilization, and storage (CCUS) have pushed the nations to move forward with capturing and sequestering 540 megatons of carbon dioxide (CO$_2$) per year by 2025 and to achieve the “carbon negative emissions.” The current statistics show that merely 5% of the total desired amount of CO$_2$ is stored. Apart from the reduction in greenhouse gases emissions, the CO$_2$ found to have extensive demand in “CO2-EOR” sector, i.e., inject CO$_2$ into depleted oil wells to enhance the oil recovery. The North American nations show the substantial capacity to capture and supply for the usages mentioned above. For such applications as well as to cover up the vast difference of storage, the adsorbents are required to be modified for the maximum removal of CO$_2$. The 2030 Agenda planned in a General Assembly at the United Nations consist of 17 Sustainable Development Goals (SDGs) to transform our world. Out of the 17 goals, Goal 6 and Goal 7 would indirectly give rise to the demand for sustainably produced activated carbon to provide clean water and energy respectively.

- Goal 6 (Clean Water and Sanitation) It has one of the primaries focusses on wastewater treatment.

- Goal 7 (Affordable and Clean Energy) It focusses to assist the generation of renewable energy.

These objectives could be accomplished by employing bio-adsorbents in pressure swing adsorption, temperature swing adsorption, and electric swing adsorption columns. Lately studied, biomass-based adsorbents have proved to remove hazardous pollutants from the industrial and
municipal wastewater (Ahmad et al., 2011). The motive is to separate CO\textsubscript{2} from pre-combustion gas or syngas, post-combustion flue gas streams, methane-rich biogas from digesters, landfills, and wastewater treatment plants, and natural gas (Songolzadeh et al., 2014). Most commonly used adsorbents in such applications are zeolites, metal organic frameworks, alkali-based dry adsorbents, metal oxides-based adsorbents, alumina, silica materials, activated carbon, ordered mesoporous carbon or carbon molecular sieves, activated carbon fibers, and graphene. In recent studies for developing the carbon-based adsorbents, it is found that moderately activated carbon shows the highest potential to capture CO\textsubscript{2} (Lee and Park, 2015). Moreover, to change the surface morphology for better selectivity and adsorptive index of the activated carbons, Pevida et al. (2008) introduced ammonia gas into the activated carbon at a temperature range of 200-800°C. The study concluded that nitrogen-containing compounds maximizes the CO\textsubscript{2} adsorption but lowers the surface area, total pore volume, and average pore diameter. Caglayan and Aksoylu (2013) used HNO\textsubscript{3}/air oxidization, Na\textsubscript{2}CO\textsubscript{3} impregnation and heat treatment under inert Helium atmosphere to stabilize the surface of commercialized activated carbon (Norit ROX 0.8). They found that ACs (AC\textsubscript{4} and AC\textsubscript{5}) those were impregnated in 10 wt. % Na\textsubscript{2}CO\textsubscript{3}, calcined, and further treated at 400°C under He atmosphere showed outstanding CO\textsubscript{2} adsorption from 0.75 wt. % to 8.19 wt.% at 1 bar. Although amine-based activated carbons are specialized for CO\textsubscript{2} capture and require low heat regeneration, the significant drawback to commercialize is due to their high costs (Yu et al., 2012).

The basis of designing systems relies on the adsorbent-adsorbate affinity, adsorption isotherms, and isosteric heat of adsorption (Sircar et al., 1999). In this study, a commercial adsorbent is compared to the bio-adsorbents on the grounds of CO\textsubscript{2} adsorption and biogas upgrading in a lab-
scale fixed bed adsorber. Several parameters such as gas residence time, flow rate, and temperature were controlled to allow better adsorption.

4.2 Material and methods

4.2.1 Design of the Experiments

The adsorption experiments were carried out in a lab – scale fixed-bed adsorber column. The schematic is represented in Fig. 4.1. The design considerations of the setup are listed in Table - 4.1. The properties of the adsorbents to be analyzed are listed in Table – 4.2. The sizing of the pipes and fittings (Swagelok™) were ¼ in. The needle-type gas valves were used. A configured biogas mixture (Praxair™) of 60% methane and 40% carbon-dioxide was used to predict the adsorption capacity of three different types of adsorbents. The gas was passed through the column filled with the adsorbents at a different pressure at 0.048 Nm³/h for 0.5 and 1 min. The gas flowmeter was calibrated to the configured biogas. The valves on the cylinder were opened to reach the pressure required for each set of experiments. All the valves were opened for a maximum of five seconds that allowed the gas to flow till it reached the 800 ml/min (~0.048Nm³/h). Since the pipe was very short hence, it took less than five seconds to achieve the specific flow rate. The valves after the pressure gauge 6 and before the vacuum gauge 7 were closed as soon as pressure and flow rate were stabilized. The valve 3 was closed when the pressure gauge 6 got to the desired pressure. The gas was held for 30 s (a stopwatch used to record the time). The valve after the pressure gauge 6 was opened that released high-pressure gas into the gas bag till the column pressure neutralized. The column was emptied using the gas syringe to pull out residual adsorbed gas. The collected gas was injected into a gas bag for further analysis. The similar procedure was used for the set of experiments for 60 s gas holding time. Prior to the experiments compressed air (~2 bar; 800
ml/min) was run through the setup to test any leak(s) where the column was filled with a bed of plastic beads and silica gel. The product gas was analyzed in a gas chromatography apparatus (GC-TCD, Agilent Technologies-6890N) and its composition was calculated using calibration curves. A gas syringe (1 L) was used to pull out the adsorbed gas to study the CO₂ concentration in the column after the experiment. A vacuum pump was run after the extraction of CO₂ to regenerate the adsorbent bed (~0.2 bar for 0.4 min) for the next set of experiments.

Table - 4.1 Design considerations of the experimental setup

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column structure</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>0.25 – 2.0 bar</td>
</tr>
<tr>
<td>Bed length, L</td>
<td>5.5 in.</td>
</tr>
<tr>
<td>Column length</td>
<td>8.0 in.</td>
</tr>
<tr>
<td>Column Diameter, D</td>
<td>0.5 in.</td>
</tr>
<tr>
<td>Column thickness</td>
<td>0.09 in.</td>
</tr>
<tr>
<td>Holding cell length</td>
<td>8.0 in.</td>
</tr>
<tr>
<td>Holding cell diameter</td>
<td>1.0 in.</td>
</tr>
<tr>
<td>Holding cell thickness</td>
<td>0.13 in.</td>
</tr>
</tbody>
</table>

The typical physical characteristics were studied for the three different types of adsorbents. The properties of commercial adsorbent were available prior to the experiment. The apparent density was estimated using ASTM D2854. The mean particle size was calculated by averaging the particle size after passing through the vibratory screen analyzer or sieve shaking.

Table - 4.2 Adsorbent properties

<table>
<thead>
<tr>
<th>Adsorbent studied</th>
<th>Weight in the column (±0.001 g)</th>
<th>Particle Density (kg/m³)</th>
<th>Bed Porosity</th>
<th>Mean Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH240-30700</td>
<td>4.72</td>
<td>475-500</td>
<td>0.25</td>
<td>Granular (&lt;0.1 mm)</td>
</tr>
<tr>
<td>DH240-30700</td>
<td>5.48</td>
<td>420-500</td>
<td>0.46</td>
<td>Granular (&lt;1.5 mm)</td>
</tr>
<tr>
<td>Commercial adsorbent</td>
<td>6.48</td>
<td>650</td>
<td>0.52</td>
<td>Granular (~1 mm)</td>
</tr>
</tbody>
</table>
4.3 Mass Transfer

Adsorption kinetics are studied assuming isosteric conditions. Since it is well known that PSA systems work well above the pressure of 4 bar, AC has proven to be the most effective choice of adsorbent. If the operating pressure is above 1.7 bar, ACs are more efficient than zeolites (Saxena et al., 2014). There are three mechanisms for the adsorption process to work:

1. Steric: the adsorption depends on the pore size distribution

2. Equilibrium: the adsorption occurs on the solid by competing for the affinity of the adsorbing components
3. Kinetic: the adsorption depends on the rates of diffusion of different components into the pore. It depends on the time of exposure of the adsorbate that results in faster desorption process from the adsorbent.

4.3.1 Mathematical model using the Langmuir model

The kinetic modeling considered for the physisorption is done by using linear isotherm by the Langmuir equation for adsorption as monolayer adsorption.

\[ Q_i = Q_{\text{max}} \left( \frac{k_L C_i}{1 + k_L C_i} \right) \] (4.1)

Where \( k_L \) is Langmuir constant, \( C_i \) is a concentration of the \( i^{\text{th}} \) gas, \( Q_i \) is the amount of the \( i^{\text{th}} \) gas adsorbed, and \( Q_{\text{max}} \) is the saturation loading capacity for the \( i^{\text{th}} \) gas adsorbed. In this study, the desorption kinetics are included. Thus, the sorption is reversible in nature. Álvarez-Gutiérrez et al. (2017) studied the kinetics of CO\(_2\) adsorption on cherry stones using Lagergren pseudo first order and pseudo-second-order model. They suggested that using pseudo-first-order model suits the study of physical adsorption of CO\(_2\) on solid adsorbents when compared to the experimental studies.

\[ \frac{dQ_i}{dt} = k_r (Q_{i,e} - Q_{i,t}) \] (4.2)

Where, \( k_r \) is the rate constant \( (\text{min}^{-1}) \), \( Q_{i,e} \) is equilibrium adsorbed gas concentration and \( Q_{i,t} \) is the adsorbed gas concentration at a time ‘t.’
A fixed bed adsorber column for a batch process is considered with the parameters calculated using the mathematical modeling is listed in Table - 4.3. The length of the column was chosen to be as represented in experimental design, such that and, the thickness of the column is neglected as the column is assumed to insulated. The porous media for the heat and mass transfer evaluation is accounted on the bio-adsorbent produced after hydrothermal carbonization. It is filled in the central zone of the column since practically the bottom, and top sections of the adsorber are packed with glass beads to support the bed of adsorbents.

The fluid (gas) flow is assumed to be laminar, incompressible and axially-dispersed along the y-direction.

The transport mechanisms occurring in the porous media are convection and dispersion. Shen and et al. (2010) estimated the diffusion parameters for the activated carbon beads to adsorb CO₂/N₂ gas mixture. The model in this work is designed considering those parameters. The mass-transfer diffusion is expressed as the mass flux ‘Nₓ’ for microporous diffusion based on the Fick’s law of diffusion as presented in the equation (4.10.b).

\[ N_i = -D_i \nabla Q_i \] (4.3)

Where, \( N_i \) s the flux of the i\(^{th} \) gas adsorbed, \( D_i \) is the diffusivity, and \( \nabla Q_i \) is the i\(^{th} \) adsorbed gas concentration gradient over an infinitesimally small distance. The tortuosity model was used to evaluate the effective diffusivity, \( D_{e,i} \) based on the porosity, ‘\( \theta_p \)’ as 0.25 and, the tortuosity was evaluated (Table – 4.3) to be 3.72.

\[ D_{e,i} = \frac{\theta_p}{\tau_{F,i}} D_{F,i} \] (4.4)
To solve the above equations, the following boundary condition was considered:

\[ N_i = 0 = -D_i \nabla Q_i \quad (4.5) \]

Substituting equation 4.1 in equation 4.7 gives;

\[ N_i = -D_i \nabla \left( Q_{i,\text{max}} \left( \frac{k_L C_i}{1 + k_L C_i} \right) \right) \quad (4.6. \alpha) \]

Integrating over the length of the bed ‘L,’ from feed side ‘f’ to the outlet side ‘o,’ and applying boundary conditions as \( C_i = C_{i,o} \);

\[ N_i = D_i \left( \frac{Q_{i,\text{max}}}{L} \right) \ln \left( \frac{1 + k_L C_{i,f}}{1 + k_L C_{i,o}} \right) \quad (4.6. \beta) \]

In porous media, permeability is a significant factor to support adsorption and desorption on the solid adsorbents. Permeability \((K)\) can be defined using Darcy’s law relating the velocity in the porous media \((u)\) and linear pressure drop \((- \frac{dP}{dx})\) for Newtonian fluid motion as;

\[ K = \mu \left( \frac{u}{\left( \frac{dP}{dx} \right)} \right) \quad (4.7) \]

Since it was assumed pressure drop to be negligible; permeability was not enforced in the mathematical modeling.

Integrating pseudo first-order model with the boundary conditions as:

At \( t = 0 \), \( Q_{i,t} = 0 \), and at \( t = \infty \), \( Q_{i,t} = Q_{i,e} \);

So, \( Q_i = Q_{i,e} \left( 1 - \exp(-k_r t) \right) \quad (4.8) \)
So according to the Langmuir’s kinetics, the final equation can be written as

\[ Q_{i,e} (1 - \exp(-k_r t)) = Q_{\text{max}} \left( \frac{k_L C_i}{1 + k_L C_i} \right) \quad (4.9) \]

The concentration of the adsorbed gas at equilibrium, \( Q_{i,e} \), bed length, \( L \), stoichiometric time, \( t_s \), and the actual time of breakthrough, \( t_b \) defines the length of the unused bed (LUB):

\[ LUB = \frac{L(t_s - t_b)}{t_s} \quad (4.10) \]

The flow of the fluid is axially dispersed in the column. The calculation was made to obtain dispersion and diffusion coefficients. Chiang et al. (2002) calculated the flow to be laminar due to very low velocity, and the Peclet number (Pe) was found to be >1. This shows that there was a convection-diffusion-reaction equation occurring in the fixed bed adsorber column. The Schmidt number (Sc) used in his work was 0.75 and is 2.0 for this model. It was suggested that Biot number if found to be low then the effect of varying the diffusion coefficient within the particles is negligible (Shahkarami, 2017). The adsorption capacity was calculated using the following equation:

\[
\text{Adsorption Capacity} \ (Q) \left( \frac{\text{mmol}}{\text{g of adsorbent}} \right) = 0.048 \left( \frac{m^3}{h} \right) \times \text{time (s)} \times (39.8 - \text{Vol. composition}) \times \rho_{nCO_2} \times 1000 \\
= \frac{3600 \times \text{Mass of the adsorbent used} \ (g) \times \text{Molarmass of CO}_2}{3600 \times \text{Mass of the adsorbent used} \ (g) \times \text{Molarmass of CO}_2}
\quad (4.11)
\]
Where the density of CO\(_2\) is 1.842 kg/m\(^3\) at NTP. The diffusivity of CH\(_4\) over CO\(_2\) is calculated using Fuller’s equation, where, \(V_d\) is the diffusion volume (for CO\(_2\) is 26.9; CH\(_4\) is 24.42), T is 298 K;

\[
D_{CH4/CO2} = \frac{1.0868 \cdot T^{1.75}}{(\frac{2}{m_{CH4}} + \frac{1}{m_{CO2}})^{0.5}} \times \left(\frac{1}{\sqrt{V_{d,CH4}}} + \frac{1}{\sqrt{V_{d,CO2}}}\right)^2
\]  

(4.12)

The viscosity for a mixture of gases at STP is defined by Sutherland-Thiesen equation (Buddenberg and Wilke, 1949). Hence, to evaluate the viscosity of the configured biogas, equation 4.13 was used using values at STP and \(y_{CH4}\), \(y_{CO2}\) are the mole fractions for CH\(_4\) and CO\(_2\);

\[
\mu = \frac{\mu_{CH4}}{1 + \frac{1.385 \mu_{CH4} y_{CO2}}{D_{CH4} \rho_{CH4} y_{CH4}}} + \frac{\mu_{CO2}}{1 + \frac{1.385 \mu_{CO2} y_{CH4}}{D_{CH4} \rho_{CO2} y_{CO2}}}
\]  

(4.13)

Freundlich isotherm is used to validate the experimental results with the predicted theory by checking the n-value. However, when the experiment was run at higher pressures the adsorption capacity reached saturation. Hence, it was not used for this study. It is expressed as:

\[
Q_l = (k_f C_{i,e})^\frac{1}{n}
\]  

(4.14.a)

or, \(\log(Q_l) = \log(k_f) + \frac{1}{n} \log(C_{i,e})\)  

(4.14.b)

where, \(k_f\) nd \(n\) are constants.

The particle to fluid mass transfer coefficient \(k_F\) is calculated using Sherwood number (Sh) relation to Schmidt number (Sc) and Reynold’s number (Re). It can be represented as:
Sh = 0.75 (Sc^{0.37} \cdot Re^{0.4}) \tag{4.15. a}

\begin{align*}
Sh &= \frac{k_F d_p}{D_{e,i}}, Sc = \frac{\mu}{\rho D_{CO2/CH4}}, Re = \frac{d_p u p}{\mu} \tag{4.15. b}
\end{align*}

This coefficient is used to derive the mathematical form of mass balance as based on the two diffusion processes:

\begin{align*}
k_F (C_i - Q_i) &= \theta_p D_{e,i} \left( \frac{\partial C_{i,t}}{\partial x} \right) + (1 - \theta_p) D_{s,i} \left( \frac{\partial Q_{i,t}}{\partial x} \right) \tag{4.16}
\end{align*}

Where, D_{s,i} is the surface diffusion coefficient (m^2/s). Since the surface area is high, D_{s,i} should be considered for the modeling.

### 4.4 Results and Discussion

The research investigated and compared the CO_2 loading in the bio-adsorbents and the commercial adsorbent. The section below explains all the results obtained after the experimental runs of KHAC700, DHAC700, and the commercial adsorbent.
Figure 4. 2 CO$_2$ adsorption in the experimental run for 30 s and 60 s gas residence time on the commercial adsorbent

Figure 4. 3 CO$_2$ adsorption in the experimental run for 30 s and 60 s gas residence time on KHAC700
Fig. 4.2 shows the total CO₂ adsorption capacity between the pressure 0.25 - 2 bar for the one-bed volume of the adsorber. The gas residence time was varied to determine the breakthrough capacities of the adsorbent used. It was noted that with an increase in pressure at 60 s, the initial adsorption was increased when compared to the 30 s curve. However, the graphs showed that gas residence time is relevant to increasing the adsorption capacities. When the pressure was increased to 0.5 bar, but the constant gas residence decreased the adsorption capacity for all the adsorbents. This is because of simultaneous desorption occurring at the adsorption sites. As the pressure increases, it plays the significant role in increasing the adsorptivity even the gas residence time remains unchanged. As Langmuir kinetics describes that multi-layer adsorption requires higher pressures and high adsorbent-adsorbate affinity, it can be noted from the loading curves that
increasing pressure has led to higher adsorption irrespective of the different gas holding time. The breakthrough of the experiments was attained very quickly. This could be possibly due to the volume of the adsorbent used in the small adsorber column. However, the length of the unused bed is negligible with respect to the holding time. The bed showed different capacities based on the pressure difference, but it attained saturation at the same pressure point.

With the increase in CO₂ adsorption, there was a significant improvement in the outlet gas. The GC-TCD results (Table 4.4) showed that in the fixed-bed adsorber there was competitive adsorption of CH₄ and CO₂. However, due to the higher affinity of the CO₂ adsorption on the carbon-based adsorbents the overall composition rose with the increasing pressure. This also aligns with the Langmuir’s kinetics. The maximum concentration of CH₄ rose from 60 vol.% to 72.5 vol.% for the commercial adsorbent. The gas compositions are similar due to the varying mass of the adsorbents used. Hence, adsorption capacity (equation 4.11) was the base of the comparison study determined using the parameters in Table 4.3.
Table - 4. 3 Calculated values and parameters for the design and mathematical model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [m]</td>
<td>Inner diameter of the column</td>
<td>0.02</td>
</tr>
<tr>
<td>L [m]</td>
<td>Length of the bed</td>
<td>0.14</td>
</tr>
<tr>
<td>vol_rate [m³/s]</td>
<td>Volumetric flow rate</td>
<td>800 ml/min = 0.043 Nm³/h</td>
</tr>
<tr>
<td>area_c [m²]</td>
<td>Area of the column</td>
<td>πDL</td>
</tr>
<tr>
<td>u [m/s]</td>
<td>Velocity</td>
<td>5.00</td>
</tr>
<tr>
<td>conc_i [mol/m³]</td>
<td>Concentration of CH₄</td>
<td>26.78</td>
</tr>
<tr>
<td>conc_ii [mol/m³]</td>
<td>Concentration of CO₂</td>
<td>17.85</td>
</tr>
<tr>
<td>θp</td>
<td>Bed Porosity</td>
<td>0.25</td>
</tr>
<tr>
<td>T [K]</td>
<td>Temperature</td>
<td>298.15</td>
</tr>
<tr>
<td>ρ [kg/m³]</td>
<td>Apparent Density</td>
<td>500</td>
</tr>
<tr>
<td>ρg [kg/m³]</td>
<td>Density of CH₄/CO₂ gas</td>
<td>1.135</td>
</tr>
<tr>
<td>K [m²]</td>
<td>Permeability</td>
<td>4.38 x 10⁻¹²</td>
</tr>
<tr>
<td>kL [g/mmol]</td>
<td>Langmuir constant</td>
<td>0.0525 (Calculated for this study)</td>
</tr>
<tr>
<td>DCH₄/CO₂ [m²/s]</td>
<td>Diffusivity (CH₄/CO₂)</td>
<td>1.8x10⁻⁵ m²/s</td>
</tr>
<tr>
<td>τf</td>
<td>Tortuosity factor,</td>
<td>3.72; ( \tau_f = \frac{\theta_p}{0.4\theta_p - 0.0328} )</td>
</tr>
<tr>
<td>τ</td>
<td>Tortuosity</td>
<td>1.375; ( \tau = 1 + [0.5(1-\theta_p)] )</td>
</tr>
<tr>
<td>μ [Pa.s]</td>
<td>Viscosity</td>
<td>4.23x10⁻⁵</td>
</tr>
<tr>
<td>Reynold’s number</td>
<td>50 (laminar)</td>
<td>Reynold’s equation ( \text{Re} = \frac{d_p u_p}{\mu} )</td>
</tr>
<tr>
<td>kF [m/s]</td>
<td>Particle to fluid mass transfer coefficient</td>
<td>1.28x10⁻³ (Calculated for this study)</td>
</tr>
<tr>
<td>kᵣ [min⁻¹]</td>
<td>Rate constant</td>
<td>0.0153 (Calculated for this study)</td>
</tr>
</tbody>
</table>
Table - 4.4 Experimental GC-TCD results for the adsorbents

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Time (s)</th>
<th>KHAC700</th>
<th>DHAC700</th>
<th>Commercial Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
<td>CH₄</td>
<td>Q co₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(vol. %) *</td>
<td>(100-</td>
<td>(mmol/g of adsorbent)</td>
</tr>
<tr>
<td>0.25</td>
<td>30</td>
<td>38.56±0.42</td>
<td>61.44</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>37.88±0.51</td>
<td>62.12</td>
<td>0.135</td>
</tr>
<tr>
<td>0.5</td>
<td>30</td>
<td>37.99±0.17</td>
<td>62.01</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>37.11±0.26</td>
<td>62.89</td>
<td>0.19</td>
</tr>
<tr>
<td>0.75</td>
<td>30</td>
<td>33.10±1.45</td>
<td>66.90</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>29.33±0.07</td>
<td>70.67</td>
<td>0.735</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>29.08±1.04</td>
<td>70.92</td>
<td>0.376</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>28.88±0.19</td>
<td>71.12</td>
<td>0.767</td>
</tr>
<tr>
<td>1.5</td>
<td>30</td>
<td>28.45±0.72</td>
<td>71.55</td>
<td>0.398</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>28.37±0.06</td>
<td>71.63</td>
<td>0.802</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>27.91±1.05</td>
<td>72.09</td>
<td>0.417</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>27.56±2.44</td>
<td>72.44</td>
<td>0.86</td>
</tr>
</tbody>
</table>

* Initial - 60.2% CH₄ and 39.8% CO₂
The figures represented above represent the similar adsorptive characteristics. The starting of the curves for KHAC700 and DHAC700 have different adsorption capacities. This difference is due to the microporosity of KHAC700 that does not allow faster adsorption in the pore sites. There is a larger amount of energy is required for the gas molecules to be pushed inside the pores. The DHAC700 has lower adsorption capacity when compared to the KHAC700. This is due to the better structural morphology caused by an increase in chemical concentration on the feedstock prior to activation. The alkaline pre-treatment assisted to increase the tortuous nature of the bio-adsorbent as well as an increase in NCCs due to the reductive reaction of KOH and hydrochar. This proves that lower chemical used during the activation is not favorable to produce an adsorbent with the high specific surface area. The alkaline pre-treatment increased the NCCs concentration that resulted in the increase in CO$_2$ adsorption capacity. The comparative study also concludes that the removal efficiency of the DHAC700 is higher than KHAC700 and commercial adsorbent since the time taken to regenerate the bed was 0.2 min for DHAC700.

The breakthrough curves for the KHAC700 has a smoother curve at 30 s whereas at 60 s there is a spike in the curve at 0.75 bar pressure. It shows that the operating parameters are inversely related. At lower pressures, gas residence time helped to increase adsorptivity while at higher pressure gas residence time had no significant role to play. This also indicates there is the complete usage of the bed length and the adsorption-desorption are appropriate at 1 bar pressure for the column in this study. With a further increase in pressure, the curve stabilized which means that the bed has obtained its equilibrium concentration.

The slight difference in the curves for DHAC700 after 1 bar pressure shows that the adsorption is favorable at higher gas residence time and continues to increase with the increase in the pressure.
The adsorption capacity at 0.75 bar for KHAC700 is higher than DHAC700 as shown in Table 4.4. This change is evident in all the adsorbents. When the pressure tends to 1 bar the adsorption kinetics suppresses the desorption kinetics, and the action becomes forward in nature. The kinetic rate constant obtained from the pseudo first-order theory confirms the same. That is the reason for the increase in the capacity at 60 s curves for all adsorbents at 0.75 bar. Once the saturation pressure is attained the column loses its capacity, and the curve becomes stagnant in nature. Lendzion-Bieluń et al. (2018) found the CO\textsubscript{2} adsorption capacity of 2.43 mmol/g after 30 min run, i.e., 0.081 mmol/g per minute. This value is lower when compared to the results for the KHAC700 at 1 bar for 60 s run, i.e., 0.86 mmol/g. This is due to the KOH assists to increase the adsorption capacity due to the chemical reactions. The pore size of the bio-adsorbent has effectively assisted the separation of the CO\textsubscript{2}/CH\textsubscript{4} molecules from the feed stream. Since the molecule size of CO\textsubscript{2} is 0.232 nm, and CH\textsubscript{4} is 0.414 nm, there is more adsorption of the CO\textsubscript{2} in the form of pore filling due to its smaller size. The competitive adsorption of CO\textsubscript{2} is also due to the faster diffusion in the pore compared to the larger CH\textsubscript{4} molecules. The carbon-based adsorbents have more affinity to the capture CO\textsubscript{2}. However, for the KHAC700, there is a chance of KOH stored on the surface of the adsorbents that participated in the competitive adsorption due to the chemisorption of CO\textsubscript{2}. The reaction of KOH and CO\textsubscript{2} is:

\[
\text{KOH (s)} + \text{CO}_2 (g) \rightarrow \text{K}_2\text{CO}_3 (s) + \text{H}_2\text{O} (g) \quad \text{(R 4.1)}
\]

The salt deposition in the pores causes the exhaustion of the KHAC700 after repeated use and requires thermal regeneration to allow the reaction of K\textsubscript{2}CO\textsubscript{3} with carbon and degrade the salt.
In order to evaluate the $k_L$, a graph of $1/Q$ vs. $1/C_f$ was plotted (Figure 4.5). The constant of the plot is 22.163, i.e., $1/(Q_{\text{max}}k_L)$. Hence, $k_L$ was found to be 0.0525 g of KHAC700/mmol of CO$_2$.

4.5 References


CONCLUSIONS AND FUTURE RECOMMENDATIONS

The biogas from anaerobic digesters has high amounts of impurities that make it unfit for use as a top-ranked fuel. As the biogas specifications differ according to the sources of the feedstock, and as the climatic conditions of every geographical area are different, there is a need to look for the best-suited method to purify this renewable resource of energy with lower energy consumption. PSA has become a preferred method to upgrade the biogas, with lower specific energy consumption and no/little extra requirement of materials other than the adsorbent. Activated carbon could be employed in the PSA systems to assist the growth of this sustainable industry due to the following reasons: (i) produced from zero-cost waste materials, they would be preferable to the commercial synthetically derived or mined adsorbents in view of generating green fuels via green processes; (ii) produced from waste biomass using hydrothermal torrefaction (220-260°C) or pyrolysis (>600°C) - further activated; and (iii) exhausted activated carbon can be beneficially amended into soil after it has lost its regeneration capacity unlike other adsorbents. Nonetheless, further study and analysis of the effects of process parameters on biogas upgrading and production of adsorbents can lead to further optimization and innovative outcomes.

The separation of gas molecules varying in the nano-scale range requires extremely precise adsorbents of low-cost hence selection of most favorable adsorbents for the PSA process becomes unclear. However, the physically or, chemically activated bio-char is the most desirable option for such applications, since it is made from zero-cost raw biomass known as bio-waste. This process started facing challenges due to the high energy requirements for carbonization and activation. The conventional method to produce activated carbon (AC) was done by using coal. There are abundant ways cited in the literature to produce activated carbon. The biomass-based nano-porous AC, bio-
adsorbent, has not yet found its potential to upgrade biogas in all aspects. The primary goal of the
study presented in this thesis was to compare the adsorptive properties of bio-adsorbents for the
separation of CO₂ from the biogas stream. The bio-adsorbents were produced after a thorough
comparison of alkaline hydrothermal carbonization (HTC) and de-ionized water HTC. The
outcomes of this environmentally sustainable method will contribute towards the objectives of
“Resource Recovery & Circular Economy Act” and “Waste Diversion Transition Act” of
Government of Ontario. In the outline, a highly microporous adsorbent was prepared from the bio-
waste, i.e., switchgrass fines. After high-temperature activation, the alkaline hydrothermal
pretreated hydrochar converted to activated carbon with an incredible pore diameter of 0.41-1.07
nm and specific surface area 339.98 m²/g. The new production method was studied and categorized
into two stages. The pretreatment step removes the conventional impregnation and subsequent
drying step prior to a chemical activation method. This method customized the production process
such that if used on a large-scale would reduce time and energy consumption.

The bio-adsorbents had a slight increase in the adsorption capacity due to the presence of slit-pores
and high surface area. The capacity was found to be 0.76 mmol/g of KHAC700 when compared
to the commercial adsorbent (0.57 mmol/g of adsorbent) after 1 minute of adsorption at 1 bar. The
performance of the DHAC700 was found to be 0.63 mmol/g of adsorbent. The separation
efficiency for DHAC700 and KHAC700 was lower than the commercial adsorbent. The loading
curves for lower gas residence time were smoother to attain the saturation limit. Since the flow
was the laminar and total volume of the bed was used in all the charts saturation occurred after 1.5
bar for the commercial adsorbent was improved for the bio-adsorbents. The curves for the different
residence time started to stabilize after 1 bar for all the adsorbents. However, KHAC700 had an increase in capacities as the pressure increased as well as with gas holding time.

The kinetic modeling for the adsorption of CO\textsubscript{2} on the bio-adsorbents was based on two parallel processes co-occurring. All types of adsorbents were characterized, and KHAC700 proved to be a practical solution to separate CH\textsubscript{4} and CO\textsubscript{2} with high surface area compared to the commercial adsorbent and excellent porosity. The experimental results for the CO\textsubscript{2} loading aligned with the modeling considering pseudo-first-order kinetic approach and Langmuir’s Isotherm. Since these adsorbents are environmentally sustainable and are economical; it could be a good choice for the upgradation industry to choose such adsorbents. It is evident that the used adsorbents have lost its’ porosity and the bed requires regeneration after every run consumption of energy increases due to this step.

Future recommendations for this study would be:

1. Modeling the thermal regeneration of the used adsorbents using the heat transfer in porous media module and setting up multicomponent diffusion process based on the design.
2. Creating a layered adsorber with multiple varieties of adsorbent packing and investigating the effects of pressure, temperature, and gas residence time.
3. Estimation of the versatility of the bio-adsorbents in the setup by introducing syngas to separate gases.
4. Modification of the setup to achieve vehicular grade fuel by addition of another loading column, new streams such as purge, bypass, and recycle, and optimizing the size. Bypassing the high-pressure product gas to a regenerated bed in a different column,
recycling the streams, and repeating this process several times (cyclic steady state) can subsequently achieve 99.9% separation as reported by a few authors in the literature study.

5. Setting up the scaled-up installation to increase CH$_4$ recovery and minimizing the number of steps and cycles required to achieve RNG specifications. For this study, a larger adsorber would have supported the case of increasing separation efficiency. The performance of the bed also depends on the activity of the pore sites and fluid-flow through the void fractions.

The particle size of the prepared bio-adsorbents was in the order of powdered activated carbon. Hence, the adsorber was close to a packed bed column with 25% bed porosity. However, usage of larger adsorbent particles with excellent properties and bed void fraction of up to 75% is recommended for a pressure swing adsorber. As cited in the literature review, industrially used PSAs are multiple columns with larger dimensions have shown to have 99.9% separation efficiency with high CH$_4$ recovery.
A.1 Safety measures

All the experiments were performed in the presence of other people in the lab. The adsorption experiments required another individual to conduct the opening and closing of valves since the pressure limit for the setup was 2.0 (±0.06) bar.

A.1.1 Disposal of Chemical and Waste

- Corrosive chemicals such as KOH solution (pH 13.25±0.13) was used to clean the BET sample holder with residual bio-oil if any. Some volatile chemicals were used for cleaning the reactors such as 70% ethanol-DI water solution and acetone. Read the Safety Data Sheets before using the chemicals and update them as necessary. The volatile and corrosive chemicals should be handled with proper personal protective equipment such as safety goggles, rubber nitrile gloves, close-toe shoes, and a lab coat. The waste after the experimentations was poured in a labeled container for re-use or disposal purposes and stored under a fume hood. The lab technician needs to be informed about the waste stored.

A.1.2 Operation of a high-pressure setup: Hydrothermal Reactor

- Prior to doing any experiment with the setup, study and consider the "pressure vessel safety policy" and "HTC experiment procedure" documents. These documents were installed in the THRN-1110, placed in the drawer related to HTC setup. The final pressure of the HTC setup is predictable using the ideal gas law equation and pressure-temperature relation for steam when the solvent considered was DI-water. The similar calculation needs to be
performed before using any other solvent. Expansion factors increase for acidic medium and oxidizers.

- The setup was monitored constantly throughout the experiments to avoid exceedance of pressure (60±0.06 bar) and temperature (±5°C).

- The residual hydrothermal solvent was found to be very acidic. The best practice is to label and store them if needed for future studies. Or, collect the liquid in a mason jar and label it for disposal. Ask the lab technician to supply with the waste disposal forms to clear out the liquid as it consists of bio-oil and acidic residual solvent.

A.1.3 Operation of a high-temperature setup: Activation Tube Reactor

- The setup heats up to 700°C (±3°C) for this study. Oven gloves, safety glasses, no loose clothing, and safety shoes were used as protective wear.

- The outlet gases from the reactor might consist of nitrogen oxides and carbon oxides. Thus, it is advisable to perform the experiments under the fume hood. The gases are very hot; hence, it is passed into a beaker with cold water to condense and react to form acids. This acidic water could be neutralized and disposed into a salt-water container or, labeled and disposed of as necessary.
## A.2 Calculations

### Table - A.2.1 Sample calculations for the in-text formulae

<table>
<thead>
<tr>
<th>Equations Used</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{bm} = \frac{1}{I + s}$</td>
<td>$q_{bm} = \frac{1}{-3.241 + 13.486} = 0.097 \text{ g}$</td>
</tr>
<tr>
<td>$S_b = \frac{q_{bm} \rho_{STP} N_{AA N2}}{M_{N2}}$</td>
<td>$S_b = \frac{0.097 \times 1.2504 \times 6.022 \times 10^{23} \times 0.162 \times 10^{-18}}{28.013}$</td>
</tr>
<tr>
<td>$r_K = \frac{2V_m \sigma \cos(\alpha)}{RT \ln \left( \frac{P}{P_0} \right)}$</td>
<td>$r_K = -0.945 \text{ nm} = 0.41 \text{ nm}$</td>
</tr>
<tr>
<td>$th = \left( \frac{-0.1399}{\ln \left( \frac{P}{P_0} \right)} - 0.034 \right)^{0.5}$</td>
<td>$th = \left( \frac{-0.1399}{\ln(0.1)} - 0.034 \right)^{0.5} = 0.16 \text{ nm}$</td>
</tr>
<tr>
<td>$r_p = r_K + th$</td>
<td>$r_p = 0.57 \text{ nm}$</td>
</tr>
<tr>
<td>$\rho_g = (Y_{CO2} \times \rho_g) + (Y_{CH4} \times \rho_g)$</td>
<td>$\rho_g = (0.398 \times 1.97 \text{ kg/m}^3) + (0.602 \times 0.656 \text{ kg/m}^3)$</td>
</tr>
<tr>
<td>$\rho_g \approx 1.175 \text{ kg/m}^3$</td>
<td>$Sc = \frac{4.23 \times 10^{-5} \text{ Pa.s}}{1.175 \text{ kg/m}^3 \times 1.8 \times 10^{-5} \text{ m}^2/\text{s}} = 2.0$</td>
</tr>
<tr>
<td>$Re = \frac{d_p u_p \rho_g}{\mu}$</td>
<td>$Re = \frac{0.0005 \text{ m} \times 5 \text{ m/s} \times 1.175 \text{ kg/m}^3}{4.23 \times 10^{-5} \text{ Pa.s}} \approx 70$</td>
</tr>
<tr>
<td>$D_{e,i} = \frac{\theta_p}{\tau_{F,i}} D_F$</td>
<td>$D_{e,i} = \frac{0.25}{3.72} \times 1.8 \times 10^{-5} \text{ m}^2/\text{s} = 1.21 \times 10^{-6} \text{ m}^2/\text{s}$</td>
</tr>
<tr>
<td>$Sh = 0.75 \left( Sc^{0.37} \cdot Re^{0.4} \right)$</td>
<td>$Sh = 0.75 \times 2^{0.37} \times 70^{0.4} = 5.03$</td>
</tr>
<tr>
<td>$Sh = \frac{k_F d_p}{D_{e,i}}$</td>
<td>$k_F = \frac{Sh \times D_{e,i}}{d_p}$</td>
</tr>
<tr>
<td>$k_F = \frac{0.75 \times 2^{0.37} \times 70^{0.4} \times 1.21 \times 10^{-6}}{0.0005}$</td>
<td>$k_F = \frac{0.75 \times 2^{0.37} \times 70^{0.4} \times 1.21 \times 10^{-6}}{0.0005}$</td>
</tr>
<tr>
<td>$k_F \approx 1.28 \times 10^{-3} \text{ m/s}$</td>
<td>$k_F = \frac{0.75 \times 2^{0.37} \times 70^{0.4} \times 1.21 \times 10^{-6}}{0.0005}$</td>
</tr>
<tr>
<td>Experimental Q (equation 4.11) for KHAC700 at 60 s and 2 bar pressure</td>
<td>$Q = \frac{0.048 \times 60 \times (0.398 - 0.2756) \times 1.824 \times 1000 \times 1000}{3600 \times 4.72 \times 44}$</td>
</tr>
<tr>
<td></td>
<td>$Q = 0.86 \text{ mmol of CO}_2/\text{g of adsorbent}$</td>
</tr>
</tbody>
</table>

Experimental Q (equation 4.11) for KHAC700 at 60 s and 2 bar pressure
<table>
<thead>
<tr>
<th>( k_L = \left( \frac{1}{Q_{\text{max}} \text{Constant}} \right) )</th>
<th>( \Rightarrow k_L = \frac{1}{0.86 \times 22.163} = 0.0525 \text{ g/mmol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{i,e}(1 - \exp(-k_r t)) )</td>
<td>( 0.767 \left( 1 - e^{-k_r \times 60} \right) )</td>
</tr>
<tr>
<td>( = Q_{\text{max}} \frac{k_L C_i}{1 + k_L C_i} )</td>
<td>( = 0.86 \left( \frac{0.0525 \times 17766 \text{ mmol/m}^3}{1 + (0.0525 \times 17766 \text{ mmol/m}^3)} \right) )</td>
</tr>
<tr>
<td>( \Rightarrow k_r = 0.0153 \text{ min}^{-1} )</td>
<td>( )</td>
</tr>
</tbody>
</table>

A.3 Quantachrome® ASiQwin™- Automated Gas Sorption Data

**Acquisition and Reduction**

© 1994-2016, Quantachrome Instruments

version 5.0

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Report</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Weight: 0.245 g</td>
<td>Instrument: Autosorb iQ Station 1</td>
</tr>
<tr>
<td>Approx. Outgas Time: 7.4 hrs</td>
<td>Final Outgas Temp.: 300 °C</td>
</tr>
<tr>
<td>Analysis gas: Nitrogen</td>
<td>Non-ideality: 6.58e-05 1/Torr</td>
</tr>
<tr>
<td>Analysis Time: 1:42 hr:min</td>
<td>Bath temp.: 77.35 K</td>
</tr>
<tr>
<td>Analysis Mode: Standard</td>
<td>VoidVol Remeasure: on</td>
</tr>
<tr>
<td>VVrm(1): ( v=0 @ t=-10 )</td>
<td>VVrm(2): ( v=0 @ t=102.5 )</td>
</tr>
<tr>
<td>VoidVol. Mode: He Measure</td>
<td>Cold Zone V: 6.36639 cc</td>
</tr>
</tbody>
</table>

**Data Reduction Parameters**

Thermal Transpiration: onEff. mol. diameter \( D \): 3.54 Å. Eff. cell stem diam. \( d \): 4.0000 mm

**Adsorbate model** Nitrogen

Temperature 77.350K

Molec. Wt.: 28.013 Cross Section: 16.200 Å² Liquid Density: 0.808 g/cc

Relative Pressure

Volume @ STP 1 / [ \( W((P_o/P) - 1) \) ]
<table>
<thead>
<tr>
<th>P/Po</th>
<th>cc/g</th>
<th>1/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0189e-01</td>
<td>260.9233</td>
<td>1.3261e+00</td>
</tr>
<tr>
<td>4.0288e-01</td>
<td>266.0568</td>
<td>2.0291e+00</td>
</tr>
<tr>
<td>5.0028e-01</td>
<td>269.1595</td>
<td>2.9760e+00</td>
</tr>
<tr>
<td>6.0081e-01</td>
<td>271.6486</td>
<td>4.4333e+00</td>
</tr>
<tr>
<td>7.0055e-01</td>
<td>273.9340</td>
<td>6.8334e+00</td>
</tr>
</tbody>
</table>

**BET summary**

Slope = 13.486 1/g  
Intercept = -3.241e+00 1/g  
Correlation coefficient, r = 0.970056  
C constant = -3.161 

Surface Area = 339.924 m²/g