MODIFICATION OF A COMMERCIAL ACTIVATED CARBON WITH NITROGEN AND BORON: HYDROGEN STORAGE APPLICATION

ARTURO IGNACIO MORANDÉ THOMPSON

Thesis submitted to the Office of Research and Graduate Studies in partial fulfillment of the requirements for the Degree of Master of Science in Engineering

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Santiago de Chile, (August, 2022)
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Santiago de Chile, (August, 2022)
To my family, friends, and teachers, who encouraged me to complete this process.
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>ACF</td>
<td>Activated carbon fiber</td>
</tr>
<tr>
<td>ACL</td>
<td>Activated carbon layer</td>
</tr>
<tr>
<td>BDH</td>
<td>Borax decahydrate</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller adsorption model</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner, Halenda method</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DBT</td>
<td>Dibenzyltoluene</td>
</tr>
<tr>
<td>DFT</td>
<td>Density-functional theory</td>
</tr>
<tr>
<td>DNEC</td>
<td>Dodecahydro-N-ethylcarbazole</td>
</tr>
<tr>
<td>HK</td>
<td>Horvath-Kawazoe model</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LOHC</td>
<td>Liquid organic hydrogen carrier</td>
</tr>
<tr>
<td>MCH</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>MDA</td>
<td>Modified Dubinin-Astakhov adsorption model</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal organic framework</td>
</tr>
<tr>
<td>NEC</td>
<td>N-ethylcarbazole</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NLDFT</td>
<td>Non-local density functional theory model</td>
</tr>
<tr>
<td>PDBT</td>
<td>Perhydro-dibenzyltoluene</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton-exchange membrane</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature (25 °C)</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific surface area (m²/g)</td>
</tr>
<tr>
<td>STP</td>
<td>Standard temperature and pressure (0 °C and 1 atmosphere)</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TOL</td>
<td>Toluene</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature-programmed decomposition</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
NOMENCLATURE

$\alpha$  MDA enthalpic factor (J/mol)
$\alpha_R$  Redlich–Peterson isotherm constant (1/bar)
at.%  Atomic percent
a.u.  Arbitrary unit
$\beta$  MDA entropic factor (J/mol K)
$b$  Langmuir isotherm constant (1/bar)
$C$  BET parameter related to the monolayer adsorption energy
$C_e$  Adsorption equilibrium concentration (bar)
$C_x$  Atomic concentration of the element $x$
$D$  Dubinin–Radushkevich isotherm constant
$\varepsilon$  MDA characteristic free energy of adsorption (J/mol)
$E_{ads}$  Adsorption energy (kJ/mol)
$E_{ACL+H_2}$  Complex energy formed by the ACL and the hydrogen molecule (kJ/mol)
$E_{(H_2)}$  Molecular energy of the isolated $H_2$ (kJ/mol)
$E_{(ACL)}$  Molecular energy of the isolated ACL (kJ/mol)
$E_B$  Binding energy of an electron (eV)
$E_K$  Kinetic energy of an emitted electron (eV)
g  Redlich–Peterson isotherm exponent
$h$  Planck constant ($6.626 \cdot 10^{-34} J \cdot Hz^{-1}$)
$I_i$  Intensity of an XPS peak associated with the i-th element (area under the peak)
$I_x$  Intensity of an XPS peak associated with the element $x$ (area under the peak)
$K_F$  Freundlich isotherm constant (wt%/bar)
$K_R$  Redlich–Peterson isotherm constant (wt%/bar)
$L$  Avogadro's constant ($6.022 \cdot 10^{23} mol^{-1}$)
m  MDA distribution parameter
$n$  Amount adsorbed at a given pressure (mol/g)
n_0  Amount of nitrogen adsorbed into the micropores (mol/g)
n_{ex}  Excess hydrogen adsorption (wt%)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_F$</td>
<td>Freundlich adsorption intensity</td>
</tr>
<tr>
<td>$n_m$</td>
<td>Monolayer capacity (mol/g)</td>
</tr>
<tr>
<td>$n_{max}$</td>
<td>MDA limiting adsorption (wt%)</td>
</tr>
<tr>
<td>$n_S$</td>
<td>Total amount of hydrogen stored in a tank (kg/m$^3$)</td>
</tr>
<tr>
<td>$p$</td>
<td>Absolute pressure (bar)</td>
</tr>
<tr>
<td>$P$</td>
<td>MDA pressure (bar)</td>
</tr>
<tr>
<td>$P_0$</td>
<td>MDA pseudo-saturation pressure (bar)</td>
</tr>
<tr>
<td>$p^o$</td>
<td>Saturation pressure of nitrogen at 77 K (bar)</td>
</tr>
<tr>
<td>$q_e$</td>
<td>Amount of adsorbate in the adsorbent at equilibrium (wt%)</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>Maximum adsorption monolayer coverage capacity (wt%)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (8.314 J/(mol K))</td>
</tr>
<tr>
<td>$r_k$</td>
<td>Kelvin radius (nm)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Coefficient of determination</td>
</tr>
<tr>
<td>$S_i$</td>
<td>Atomic sensitivity factor of the i-th element</td>
</tr>
<tr>
<td>$S_x$</td>
<td>Atomic sensitivity factor of the element $x$</td>
</tr>
<tr>
<td>$t$</td>
<td>Monolayer thickness (nm)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature ($^\circ$C)</td>
</tr>
<tr>
<td>$v$</td>
<td>Frequency (Hz)</td>
</tr>
<tr>
<td>$V_a$</td>
<td>Adsorption volume (cm$^3$/g)</td>
</tr>
<tr>
<td>$V_{free}$</td>
<td>Adsorption free volume (cm$^3$/g)</td>
</tr>
<tr>
<td>$V_{v,sys}$</td>
<td>Total void volume of the adsorption system: $V_a + V_{free}$ (cm$^3$/g)</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Mesopore volume (cm$^3$/g)</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Micropore volume (cm$^3$/g)</td>
</tr>
<tr>
<td>$w$</td>
<td>Pore diameter (nm)</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>$\rho_{He}$</td>
<td>Skeletal or helium density of an adsorbent (kg/m$^3$)</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>Bulk density of an adsorbent (kg/m$^3$)</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Gas phase density (kg/m$^3$)</td>
</tr>
<tr>
<td>$\sigma_m$</td>
<td>Molecular cross-sectional area (nm$^2$/molecule)</td>
</tr>
<tr>
<td>$\phi_{sp}$</td>
<td>Work function of a spectrometer (eV)</td>
</tr>
</tbody>
</table>
ABSTRACT

In this study, a commercial activated carbon with a specific surface area (SSA) of 1678 m$^2$/g was studied and modified to store hydrogen through physical adsorption at 77 K. For this purpose, different modification methods were considered. Helium treatments at 200 and 400 °C were applied to reduce the concentration of oxygenated functional groups on the surface of the original sample; ammonia modifications at 400, 500 and 600 °C were carried out to produce nitrogen-doped samples; and borax decahydrate impregnations were performed to dope the samples with boron. A total of 13 samples were produced by applying these three main modifications methods in different orders. These samples were analyzed and characterized by nitrogen adsorption/desorption isotherms, temperature-programmed decompositions, X-ray photoelectron spectrosopies, and hydrogen adsorption isotherms. In addition, the Dubinin-Astakhov adsorption model was applied to extrapolate the hydrogen adsorption experimental data up to 100 bar pressure, and a density-functional theory model was developed to analyze the effect of the nitrogen functionalities on hydrogen adsorption. Based on the results, it was concluded that the best modification procedure was the helium treatment at 400 °C followed by an ammonia treatment at 500 °C, increasing the hydrogen adsorption from 1.98 to 2.34 wt%. All B-doped samples reduced their hydrogen adsorption due to the loss of SSA, although the adsorption per area (i.e., wt%/SSA) increased.

Keywords: Hydrogen adsorption, Activated carbon, Nitrogen, Boron, Doping, Ammonia, Borax decahydrate, Dubinin-Astakhov adsorption model.
RESUMEN

En esta investigación, se estudió y modificó un carbón activado comercial con una superficie específica (SSA) de 1678 m$^2$/g con la finalidad de almacenar hidrógeno mediante la adsorción física a 77 K. Para este propósito, se consideraron diferentes métodos de modificación. Se llevaron a cabo tratamientos con helio a 200 y 400 ºC para reducir la concentración de grupos funcionales oxigenados en la superficie de la muestra original; se realizaron modificaciones con amoníaco a 400, 500 y 600 ºC para producir muestras dopadas con nitrógeno; y se realizaron impregnaciones con bóxar decahidratado para dopar las muestras con boro. Se produjeron un total de 13 muestras mediante estos tres métodos de modificación, los que fueron aplicados en diferentes órdenes. Las muestras se analizaron y caracterizaron mediante isoterma de adsorción/desorción de nitrógeno, descomposiciones programadas por temperatura, espectroscopías fotoeléctronicas de rayos X e isoterma de adsorción de hidrógeno. Adicionalmente, se aplicó el modelo de adsorción de Dubinin-Astakhov para extrapolar los datos experimentales de adsorción de hidrógeno hasta una presión de 100 bares, y se desarrolló un modelo de teoría del funcional de la densidad para analizar el efecto de las funcionalidades nitrogenadas en la adsorción de hidrógeno. En base a los resultados, se concluyó que el mejor procedimiento de modificación fue el tratamiento con helio a 400 ºC seguido de un tratamiento con amoníaco a 500 ºC, lo que aumentó la adsorción de hidrógeno desde un 1,98% a un 2,34% en peso. Además, todas las muestras dopadas con boro redujeron su adsorción de hidrógeno debido a la pérdida de superficie específica, aunque aumentó la adsorción por unidad de área, es decir, % en peso/SSA.

Palabras Claves: Adsorción de hidrógeno, Carbón activado, Nitrógeno, Boro, Dopaje, Amoníaco, Bórax decahidratado, Modelo de adsorción de Dubinin-Astakhov.
1. **INTRODUCTION**

Hydrogen gas is an energy vector that is gaining relevance due to its potential to reduce carbon dioxide emissions in different areas. Nowadays, hydrogen is produced almost completely from fossil sources, but if it is produced from low emission energies (such as renewable, biomass, nuclear, and fossil fuels with carbon capture and storage), it could become the key element for the reduction of the worldwide carbon footprint. This energy vector can be applied in the fields of industry (e.g., oil refining, ammonia production, methanol production, and steel production), space heating (e.g., boilers, space heaters, and heat and power applications), transportation (e.g., buses, trucks, cars, ships, and airplanes), and power generation (e.g., gas turbines, fuel cells, and energy storage) (Chapman *et al.*, 2019). Because of its wide possible applications, it will play a major role in the energy and production systems of the future.

The main benefits of hydrogen are related to its energy carrier property and how its energy can be harnessed. On the one hand, using hydrogen as a fuel has no direct greenhouse gas emissions. Then, hydrogen can be favorable in places where emissions and pollutants are restricted or where they cause problems, such as cities and facilities with poor ventilation (e.g., warehouses and tunnels). On the other hand, hydrogen can store great amounts of energy for long periods, which could help stabilize the intermittency of renewable energy sources, storing energy in periods of lower demand and higher production, and then releasing it when required (e.g., solar energy storage to supply electricity at night and energy storage for vehicles).
The hydrogen value chain has four basic parts: production, storage, distribution, and utilization (Frischauf et al., 2013). This study is focused on the storage of hydrogen, which is one of the most complex parts of the value chain due to the low density of this gas. Specifically, the storage of hydrogen through the process of physical adsorption on activated carbons is studied.

1.1 Hydrogen Storage Technologies

Hydrogen has a high gravimetric energy density (120 MJ/kg) in comparison to other fuels like diesel (43.4 MJ/kg) or gasoline (41.6 MJ/kg), but its volumetric energy density depends on the storage system, and it is much lower (2.8 to 8.6 MJ/L) than the volumetric energy density of diesel (36.8 MJ/L) and gasoline (30.8 MJ/L) (Stetson et al., 2016). With the aim of improving the hydrogen storage density, the U.S. Department of Energy established an onboard hydrogen storage target of 0.065 kg H₂/kg system and 0.050 kg H₂/L system for Light-Duty vehicles (U.S. Department of Energy, n.d.). When talking about the storage system, the vessel or tank, pipes, valves, and other components required for the storage are included.

The storage of hydrogen can be done with different technologies, which can be classified into three main categories: physical storage, physical adsorption, and chemical storage (Andersson & Grönkvist, 2019). Also, the physical adsorption and chemical storage can be classified as material-based storage, because hydrogen is stored by the interaction with another material or molecule. The storage methods of these last two categories are under development and investigation, while the physical storage has mature solutions that are used on the market. The different storage technologies are described below.
1.1.1 Physical storage

The physical storage implies that the hydrogen is stored in its molecular form as a gas or liquid (Andersson et al., 2019). It is stored inside a vessel or tank, and its density depends on the storing pressure and temperature. Figure 1-1 shows how the hydrogen density (kg/m³) depends on the storage temperature and pressure. In this case, the hydrogen density is presented on the vertical axis, the temperature is on the horizontal axis, and the pressure is expressed as isobars of 0.5, 10, 35, 50, and 70 MPa. As can be seen from Figure 1-1, the tendency is that at lower temperatures and higher pressures the density of hydrogen increases.

Figure 1-1: Hydrogen density versus temperature for several storage pressures (Stetson et al., 2016)
There are four ways of storage for this category: compressed gaseous hydrogen, cold-compressed hydrogen, cryo-compressed hydrogen, and liquid hydrogen (Stetson et al., 2016). Nowadays, compressed and liquid hydrogen are the main storage solutions that are used in the market.

1.1.1.1 Compressed gaseous hydrogen

Hydrogen is stored in the near ambient temperature range under pressures up to 700 bar (red region in Figure 1-1). Carbon fiber composite cylinders or Type IV vessels are used to store hydrogen at pressures up to 350 or 700 bar in automotive applications due to their lower weight compared to other types of vessels. These cylinders can store 5.4 and 4.4 wt% (weight percent) of hydrogen, with 17.7 and 25.0 kg of hydrogen per m$^3$ of system volume for 350 bar and 700 bar cylinders, respectively (Stetson et al., 2016). The Toyota Mirai has a 700 bar storage tank of 122.4 L and reaches 5.7 wt% of stored hydrogen. Some disadvantages of this storage method are the low volumetric density, the energy required for compression (around 15% of hydrogen lower heating value), and safety concerns (Sinigaglia et al., 2017).

1.1.1.2 Liquid hydrogen

To store hydrogen in liquid state it is necessary to cool it to 20 K, reaching a density of 71 kg/m$^3$ at atmospheric pressure (blue region in Figure 1-1). The vessels used are insulated to reduce the boil-off or evaporation of hydrogen and they work with pressures of around 1 bar (Stetson et al., 2016). Despite the higher density of liquid hydrogen, the weight and size of the vessel limit the hydrogen density of the system to 5.6 wt% and 23.5 kg H$_2$/m$^3$ (Ahluwalia et al., 2016). The disadvantages of this storage method are the high amounts of energy required for liquefaction (around 30% of hydrogen lower heating value), the high cost of the vessels, and the losses due to evaporation (0.1 to 1% per day) (Sinigaglia et al., 2017).
1.1.1.3 Cryo-compressed hydrogen

This storage system is under development and operates at temperatures below 150 K with pressures up to 350 bar (green region in Figure 1-1). The vessels used for cryo-compressed hydrogen storage are insulated and can withstand high pressures (Stetson et al., 2016). A vessel operating at 240 bar and 21 K can reach a hydrogen density of 81 kg/m$^3$, and depending on the design of the tank and the operation conditions (pressure and temperature) the gravimetric capacity of the system is in the range of 5.5 to 9.2 wt% and the volumetric capacity is in the range of 41.8 to 44.7 kg H$_2$/m$^3$ (Ahluwalia et al., 2016). The advantages of this system are the flexibility to operate with hydrogen under different conditions (liquid, compressed at room temperature, and cryo-compressed), the evaporation losses are reduced due to the higher pressure resistance, and if the vessel operates with hydrogen compressed at 200 bar at 80 K the work required is around the 20 to 30% of the liquefaction work (Stetson et al., 2016). A disadvantage could be the major complexity of the system.

1.1.1.4 Cold-compressed hydrogen

This storage system works with the same principles as the cryo-compressed system but in a temperature range of 150 to 230 K and with pressures up to 500 bar (Stetson et al., 2016). Cold-compressed hydrogen can be found in the orange region in Figure 1-1.

1.1.2 Physical adsorption

Adsorption is an exothermic process in which an atom, ion, or molecule (the adsorbate) is attracted and retained by the surface of a solid (the adsorbent), while
desorption is the opposite process. The adsorbate is in a fluid or suspended state and reaches the surface of the adsorbent through flow and diffusion. Figure 1-2a presents a schematic diagram of the adsorption process on a flat surface, while Figure 1-2b depicts the adsorption of adsorbates on the internal and external surfaces of a porous adsorbent.

Figure 1-2: a) Schematic diagram of the adsorption process (Moon and Palaniandy, 2019). b) Representation of adsorption on a porous adsorbent (Zbair and Bennici, 2021)
The amount of hydrogen stored by an adsorbent (adsorption capacity) can be expressed as: “(mass of adsorbed H₂)/(mass of the adsorbent + mass of adsorbed H₂)” or “(mass of adsorbed H₂)/(mass of the adsorbent)”. In this document, the second expression is defined as weight percent (wt%). This definition excludes the weight of the rest of the system (vessel, piping, valves, etc.). In addition, the volumetric storage can be calculated considering the density of the adsorbent. Then, storage can be presented as the fraction between the mass of adsorbate and the total volume.

Depending on the nature of the interaction between the adsorbate and adsorbent, adsorption can be classified into physical or chemical. Van der Waals forces are the interactions involved in the physical adsorption or physisorption, while chemical bonds are the interactions that drive the chemical adsorption or chemisorption. Because the Van der Waals forces implied in physical adsorption (<10 kJ/mol) are weaker than chemical bonds implied in chemical adsorption (50 to 100 kJ/mol), physisorption is easily reversible in comparison to chemisorption. But this has a drawback: a lower hydrogen storage density due to the weaker interactions (Boateng & Chen, 2020). To overcome this drawback and have a higher density of hydrogen stored by physical adsorption (adsorption from now on) cryogenic temperatures are required. Generally, 77 K is the temperature used for cryogenic adsorption, which is the boiling point of liquid nitrogen (Andersson et al., 2019). Also, adsorption at room temperature (RT) is studied, but pressures above 100 bar are required to achieve acceptable amounts of hydrogen stored. For comparison, Geng et al. (2015) reached adsorption of 1.9 wt% at 77 K and under 1 bar pressure using activated carbon, while the same material adsorbed 1.5 wt% at 298 K and 165 bar.
The materials studied for hydrogen adsorption are porous materials that have large specific surface areas (surface area per unit of mass expressed in m$^2$/g) and high pore volumes (volume of pores per unit of mass expressed in cm$^3$/g). Generally, the adsorbents with higher specific surface area (SSA) and pore volume have a better performance on hydrogen adsorption. Some materials have SSAs higher than 2000 m$^2$/g and pore volumes above 1.5 cm$^3$/g. Examples of adsorbents are porous carbon-based materials, such as activated carbons (AC), carbon nanotubes (CNT), graphene, and activated carbon fibers (ACF); metal-organic frameworks (MOF); porous polymeric materials; zeolites; among others (Andersson et al., 2019). Depending on the adsorbent, adsorption temperature, and pressure range, the storage of hydrogen by adsorption can reach values in the ranges of 0.2 - 8.2 wt%, and 15.2 - 39.3 kg/m$^3$ (Lozano-Castelló et al., 2013).

The adsorption process is carried out inside a vessel (usually in a laboratory instrument) filled with the adsorbent, and the hydrogen enters at the desired pressure and temperature. In scientific studies, the adsorption process is carried out at a fixed temperature, and the pressure is increased in small steps while the amount of hydrogen adsorbed is determined. With these data, the adsorption isotherm can be constructed and plotted with the amount adsorbed on the vertical axis and the pressure on the horizontal axis. The desorption process can also be included in the isotherm. An example of hydrogen adsorption isotherms performed on activated carbons at 77 K is presented in Figure 1-3.
Figure 1-3: Hydrogen adsorption isotherms on different activated carbons (Heo & Park, 2015)

From the isotherms, information such as the maximum adsorption or the adsorption mechanism can be obtained. The two main adsorption mechanisms are explained by the Langmuir and Freundlich models. These are empirical models that describe the adsorption isotherms with a mathematical equation. The Langmuir isotherm model assumes monolayer adsorption, whereas the Freundlich model is not limited to the monolayer coverage and can describe a multilayer adsorption mechanism. These models can be fitted to an experimental isotherm, and if they have a good fit with the data, it can be assumed that the adsorption follows one or the other mechanism. There are many other isotherm models, including the Redlich–Peterson model, which is a hybrid isotherm between the Langmuir and Freundlich models, and the Dubinin-Astakhov model (Foo & Hameed, 2010).
1.1.3 Chemical storage

This storage mechanism is based on the formation of chemical bonds between hydrogen and other molecules or compounds. Chemical storage can be divided into two main groups: metal hydrides and chemical hydrides (Andersson et al., 2019).

1.1.3.1 Metal hydrides

Metal hydrides are compounds that contain metal atoms, in which hydrogen is stored by chemical bonds. Due to the nature of the bonds, metal hydrides can achieve higher hydrogen storage densities in comparison to physical adsorption, but more energy is required to release hydrogen when it is needed. The main ways to release hydrogen are the thermolysis and hydrolysis reactions. Thermolysis consists of heating the metal hydride to a certain temperature (endothermic reaction) to release the hydrogen, while in hydrolysis the metal hydride reacts with water (exothermic reaction) to release the hydrogen. Thermolysis is the most common mechanism for releasing hydrogen from metal hydrides. Just like in physical adsorption, the storage with metal hydrides is carried out inside a vessel. There are three types of metal hydrides: elemental metal hydrides, intermetallic hydrides, and complex metal hydrides (Andersson et al., 2019).

a) Elemental metal hydrides

Elemental metal hydrides are binary compounds made of hydrogen and a metallic element. The most promising elemental metal hydrides are magnesium hydride (MgH₂) and aluminum hydride (AlH₃). Magnesium hydride can achieve a hydrogen storage density of around 6.0 wt% and 86 kg/m³. Its main drawback is that the bond between hydrogen and magnesium is strong (75 kJ/mol), and the dehydrogenation reactions are slow. To overcome this drawback, temperatures above 300 °C are required for the release of hydrogen. Aluminum hydride has a theoretical hydrogen
storage capacity of 10.1 wt%, the bond between aluminum and hydrogen is weak (7 kJ/mol), and the dehydrogenation reactions are fast at 100 °C. The main drawback is the extreme pressure required to form the aluminum hydride (Andersson et al., 2019).

b) Intermetallic hydrides

In intermetallic hydrides, an alloy of two elements is used to form the hydride (AₓBᵧHₓ). The element ‘A’ has a strong binding energy with hydrogen, while the element ‘B’ has weaker binding energy with hydrogen. The purpose of this is to reach a hydrogen storage property that is intermediate to the properties of the two constituent elements. Despite the low gravimetric storage that these materials can reach (generally less than 2 wt%), their volumetric density can be as high as 65 kg/m³, which is favorable for stationary applications. TiFe hydride has a hydrogen storage capacity of 1.9 wt% (Andersson et al., 2019), and LaNi₅H₆ has a gravimetric capacity of 1.2 wt% and a volumetric capacity of 87.0 kg/m³ (Marinelli & Santarelli, 2020).

c) Complex metal hydrides

In complex metal hydrides, hydrogen is part of a complex anion that is bonded to a metallic cation. Complex metal hydrides are lighter than intermetallic hydrides, which is favorable for vehicle applications. The main drawbacks of complex metal hydrides are the requirement of high temperatures and the presence of catalysts or additives to carry out the dehydrogenation process. The main complex anions used for complex metal hydrides are the alanates ([AlH₄⁻]), borohydrides ([BH₄⁻]), and the amides ([NH₂⁻]).

Sodium alanate (NaAlH₄) with Ti-based catalyst has a hydrogen storage capacity of 4 wt% and 54 kg/m³. Borohydrides have higher binding energy with hydrogen in
comparison to alanates, then high temperatures are required for dehydrogenation (generally above 300 °C). To overcome this problem, borohydrides are mixed with other metal hydrides. This reduces the energy required for the dehydrogenation process. An example of this is the mixture of LiBH₄ with MgH₂. This mixture, with the help of a catalyst, can reach a hydrogen storage capacity of 9.1 wt% and 68 kg/m³. Finally, amide storage systems consist of a metal amide ([M][NH₂]) mixed with an elemental hydride. The purpose of the elemental hydride is to prevent the release of ammonia instead of hydrogen during thermolysis, but traces of ammonia are released anyway. This is inconvenient because there is a loss of the active material in every cycle of operation, and ammonia poisons PEM (proton-exchange membrane) fuel cells. A mixture of LiNH₂, MgH₂, LiBH₄, and ZrCoH₃ has a hydrogen storage capacity of 4.5 - 5.2 wt%, with a dehydrogenation and hydrogenation temperature of 150 °C. A hydrogen storage density of 54 kg/m³ can be achieved with a mixture of LiNH₂ and MgH₂ (Andersson et al., 2019).

1.1.3.2 Chemical hydrides

In chemical hydrides, hydrogen is bonded to light and non-metallic elements, such as carbon, nitrogen, boron, and oxygen. Some examples of chemical hydrides that can be used to store hydrogen are methanol, ammonia, formic acid, and liquid organic hydrogen carriers. Most of these chemical hydrides are liquid under normal conditions, which simplifies their storage and transport. Additionally, methanol, ammonia, and formic acid are chemicals that are used beyond the storage of hydrogen, and nowadays they are widely produced from natural gas. The production, handling, and transport of these chemicals are already developed today (Andersson et al., 2019).
a) Methanol

Methanol (CH\textsubscript{3}OH) is a liquid that has a hydrogen storage density of 12.5 wt\% and 99 kg/m\textsuperscript{3}. It can be produced through the hydrogenation of carbon dioxide at temperatures around 220 – 280 °C and pressures between 10 and 80 bar. The CO\textsubscript{2} hydrogenation reaction is exothermic, and then a small or no input of heat is required to carry out the reaction. Hydrogen can be released from methanol by a steam reforming reaction, partial oxidation reaction, or thermolysis. The steam reforming of methanol releases three moles of hydrogen per mole of methanol (water provides one mole of hydrogen), while the other reactions release only two moles of hydrogen. The steam reforming reaction requires temperatures between 230 and 330 °C (it is an endothermic reaction), and Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts are used (Andersson \textit{et al.}, 2019).

b) Ammonia

Ammonia (NH\textsubscript{3}) is a gas that liquefies at 10 bar and RT, and in its liquid state it has a hydrogen storage density of 17.7 wt\% and 123 kg/m\textsuperscript{3}. A huge advantage of ammonia is that natural gas-based ammonia plants can be easily retrofitted to use hydrogen produced from water electrolysis. Ammonia is mainly synthesized by the Haber-Bosch process, which is an exothermic reaction that takes place in the ranges of 300 - 550 °C and 200 - 300 bar. The rejected heat can be used to produce energy through steam, and this energy can be used for compression, achieving a highly efficient process. Despite these advantages, the dehydrogenation of ammonia is a challenge. Hydrogen is released from ammonia through a thermolysis reaction that requires high temperatures (above 650 °C) and the presence of catalysts, which are expensive and/or under development (Andersson \textit{et al.}, 2019).
c) Formic acid

Formic acid (HCO$_2$H) has a hydrogen storage density of 4.4 wt% and 53 kg/m$^3$. The advantage of this chemical hydride is that the dehydrogenation process can be carried out at temperatures near RT, releasing hydrogen and CO$_2$ at pressures above 1000 bar. The high-pressure hydrogen release is attractive for applications such as hydrogen fueling stations, but to take advantage of this, a high-pressure CO$_2$ separation process must be developed. Formic acid can be produced by CO$_2$ hydrogenation, a reaction that must be performed in a basic solution with a homogeneous catalyst. “The base, which is generally an amine, reacts with the produced formic acid as it is formed to yield a formate salt, thus driving the equilibrium towards formic acid production” (Andersson et al., 2019, p. 11909). There is another drawback in the production process, the separation of the formic acid from the basic solution and the catalyst is a difficult and energy-intensive process (Andersson et al., 2019).

d) Liquid organic hydrogen carriers

Liquid organic hydrogen carriers (LOHCs) “are different materials characterized by their reversible dehydrogenation and hydrogenation and their liquid state in both hydrogenated and dehydrogenated forms” (Andersson et al., 2019, p. 11910). LOHCs in their dehydrogenated form are aromatic compounds, and hydrogen is incorporated into them through the saturation of carbon-carbon bonds. “The most well-investigated LOHCs are (hydrogenated and dehydrogenated forms) methylcyclohexane and toluene (MCH-TOL); dibenzyltoluene and perhydro-dibenzytoluene (DBT-PDBT); and N-ethylcarbazole and dodecahydro-N-ethylcarbazole (NEC-DNEC)” (Andersson et al., 2019, p. 11910). The hydrogen storage densities reached with these compounds are in the ranges of 5.8 - 6.2 wt% and 47 - 64 kg/m$^3$. The dehydrogenation reaction is catalyzed with supported noble metal catalysts, and it is endothermic, requiring temperatures between 200 and 300
°C depending on the LOHC. Supported noble metal catalysts are also applied for the hydrogenation process, and the required pressures are in the range of 10 - 50 bar with temperatures between 130 and 200 °C (Andersson et al., 2019).

### 1.1.4 Comparison of storage technologies

Table I-1 summarizes the hydrogen storage densities of the different storage methods.

<table>
<thead>
<tr>
<th>Storage Method</th>
<th>Gravimetric Hydrogen Storage Density (wt%)</th>
<th>Volumetric Hydrogen Storage Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed H₂</td>
<td>4.4 - 5.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.7 - 25.0&lt;sup&gt;a&lt;/sup&gt; (23.3 - 39.2)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Liquid H₂</td>
<td>5.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>23.5&lt;sup&gt;a&lt;/sup&gt; (71.0)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cryo-compressed H₂</td>
<td>5.5 - 9.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>41.8 - 44.7&lt;sup&gt;a&lt;/sup&gt; (40.0 - 81.0)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Physical adsorption</td>
<td>0.2 - 8.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.2 - 39.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Elemental metal hydrides</td>
<td>6.0 - 10.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>86.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Intermetallic hydrides</td>
<td>1.2 - 2.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>65.0 - 87.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Complex metal hydrides</td>
<td>4.0 - 9.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>54.0 - 68.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methanol</td>
<td>12.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>99.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ammonia</td>
<td>17.7&lt;sup&gt;b&lt;/sup&gt;</td>
<td>123.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Formic acid</td>
<td>4.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>53.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>LOHCs</td>
<td>5.8 - 6.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>47.0 - 64.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Including the vessel, piping, and the rest of the storage system. <sup>b</sup> Hydrogen density.
1.2 Hydrogen Storage on Activated Carbons

Activated carbons are used in many fields of the industry, such as water treatment, chemical processing, gas storage, gas separation, catalysis, solvent recovery, among others (Baker et al., 2003). In this study, the hydrogen storage on activated carbons is analyzed. First, it is important to understand what activated carbons are, their properties, and how they store hydrogen.

1.2.1 Definition and production of activated carbons

Activated carbons are carbon-based materials with an amorphous and highly developed porous structure, and with different types of oxygenated functional groups attached to the edges of graphitic planes (González-García, 2018). Graphitic or graphene planes consist of multiple carbon atoms bonded together and arranged in a hexagonal lattice, forming a flat layer. Figure 1-4 represents the amorphous structure of activated carbons, which are made up of graphitic planes (also known as aromatic planes) that are broken, twisted, and cross-linked, forming slit and cylindrical pores (Moseley et al., 2018).
The specific surface area and pore volume are one of the most important parameters to measure the porous development of activated carbons. Generally, the SSA of these materials is in the range of 600 to 2000 m$^2$/g, with some exceptions over 2500 m$^2$/g, and the total pore volume is in the range of 0.5 to 2 cm$^3$/g. Depending on their size, pores are classified into macropores, mesopores, and micropores. Macropores are pores greater than 50 nm in diameter, mesopores are in the range of 2-50 nm, and micropores are the ones smaller than 2 nm. Based on this, the total pore volume of activated carbon is made up of the macropore, mesopore, and micropore volumes, but for highly porous materials, such as activated carbons, the macropore volume is negligible.

Activated carbons are produced in four formats: powder, pellet, granular, and honeycomb structure (Figure 1-5). Pellet and honeycomb activated carbons are made from the extrusion of powder-activated carbon mixed with a binder. The main activated carbon formats on the market are powder, granular, and pellet.
Activated carbons are produced from a precursor material, which is subjected to an activation process to generate the porous material. There are different types of precursors, and their characteristics will define the properties of the final activated carbons. The precursor should be inexpensive and nonhazardous for nature, and high amounts of fixed carbon and low ash content are required to develop high specific surface area (González-García, 2018). Activated carbons can be made from biomass (e.g., coconut, wood, rice husk, olive stones, etc.), polymers, coals, among other materials with high carbon contents (González-García, 2018; Lozano-Castelló et al., 2013).

Figure 1-5: Different formats of activated carbons: a) powder, b) pellet, c) granular, and d) honeycomb (Source: http://www.hnlywater.com/)
Some precursors need a carbonization process or pyrolysis before the activation procedure (generally biomass or lignocellulosic materials require this process). Pyrolysis is a degradation process of organic materials caused by a heat flux, which breaks down polymers and releases them as hydrocarbon gases (volatiles). This process aims to increase the carbon content of the precursor by removing moisture and the produced volatiles, obtaining, as a result, a fixed carbonaceous skeleton (González-García, 2018). In the pyrolysis process, materials are exposed to high temperatures (generally over 600 °C) with or without the presence of an inert atmosphere, and with a controlled heating rate and residence time.

After the precursor is selected and carbonized (if required), the activation process is applied. The activation process aims to generate new pores, increase their number, and increase the size of the existing ones (Lozano-Castelló et al., 2013). There are two possible activation procedures: physical and chemical. On the one hand, physical activation is a controlled gasification of the precursor at temperatures between 800 and 1000 °C under a high oxidizing atmosphere. The main oxidizing agents used are carbon dioxide, water steam, and oxygen. On the other hand, in chemical activation, the precursor is impregnated with a chemical activation agent (e.g., H₃PO₄, H₂SO₄, HNO₃, ZnCl₂, NaOH, KOH, etc.), then it is treated at high temperatures (400 to 1000 °C) under a controlled atmosphere, and finally, it is washed to remove the chemical agent. The role of the chemical agent is to develop the porous structure by the degradation and dehydration of the precursor. Some advantages of the chemical activation over the physical activation are the lower pyrolysis temperatures and times, and higher production yields, and it can be applied to high ash content materials without drawbacks. Some disadvantages are the need for additional procedures (impregnation and washing stage), and the corrosiveness of the activating agents (González-García, 2018; Lozano-Castelló et al., 2013).
1.2.2 Hydrogen adsorption on activated carbons

As mentioned earlier, the adsorption process takes place because of the Van der Waals interactions between the adsorbate and the adsorbent, in this case, between hydrogen and activated carbons. The force of attraction between hydrogen and an activated carbon depends on the adsorption enthalpy between them. A higher adsorption enthalpy implies higher adsorption and storage of hydrogen. Generally, the adsorption enthalpy of hydrogen on activated carbons is lower than 10 kJ/mol (Boateng et al., 2020). This is why the low hydrogen storage reached at low pressures and RT.

In addition to the adsorption enthalpy between the adsorbate and the adsorbent, other factors influence the adsorption and storage of hydrogen on activated carbons. Factors such as the specific surface area, micropore volume and size, density of the adsorbent, the presence of functional groups, and dopants must be considered.

1.2.2.1 Surface area effect

Because adsorption is a surface process, the higher the SSA, the higher adsorption. Studies presented by Xia et al. (2007), Panella et al. (2005), and Klechikov et al. (2015) show positive correlations between the SSA and the hydrogen adsorbed on activated carbons and other carbonaceous materials. This tendency is valid for adsorptions at 77 K and RT. The only difference between the correlations at 77 K and RT is the trend line slope, where the slope of the correlation at 77 K is steeper than the slope at RT (see Figure 1-6). It is important to clarify that this tendency is valid for materials of the same nature. For example, a doped activated carbon can achieve higher hydrogen adsorption than an undoped activated carbon with higher
SSA. Also, the total pore volume is related to the SSA. Then, the total adsorption also depends on the total pore volume.

Figure 1-6: a) Hydrogen adsorption isotherms for graphene samples and activated carbon (red isotherm) at 77 K, and b) hydrogen adsorptions at ambient temperature with 120 bar pressure, and 77 K with 50 bar pressure (Klechikov et al., 2015)

1.2.2.2 Micropore effect

Another important parameter for hydrogen adsorption on activated carbons is the size and volume of the micropores. Xia et al. (2007) and Panella et al. (2005) found positive linear correlations between hydrogen adsorption at 77 K and the micropore volume. Specifically, Xia et al. (2007) claim that micropores smaller than 1 nm have a better correlation with the hydrogen adsorbed at 77 K in comparison to micropores with diameters between 1 and 2 nm. Likewise, Panella et al. (2005) present a linear relationship between the volumes of micropores smaller than 1.3 nm and the adsorption of hydrogen at 77 K in carbon materials (see Figure 1-7). Then, the larger the micropore volume, the greater hydrogen adsorption, with special emphasis on narrow micropores (< 1 nm).
A more detailed study about this scope was carried out by Geng et al. (2015). The authors developed different samples of activated carbons made from corn cob and activated with KOH, and their hydrogen adsorption properties were studied at 77 K and RT with pressures up to 165 bar. Based on the hydrogen adsorption data, the authors concluded that ultra-micropores (0.65 – 0.85 nm) could be the most effective pores for hydrogen adsorption at 77 K and low pressures (i.e., 1 bar), while micropores in the 0.85 – 2 nm size range are more effective for the adsorption of hydrogen at higher pressures. Regarding adsorption at RT, there was no clear effect of the pore size in the adsorption of hydrogen, whereas the SSA and total pore volume showed a relevant effect.

There are two reasons behind the effect of the micropores in the adsorption of hydrogen. The first reason is that a higher micropore volume implies a higher SSA. This can be understood with the following example. Figure 1-8 shows two cubes of
1 cm³ that have pores of different sizes. Comparing the surface area that is inside the pores, the first cube (the one with wider pores) has an internal area of about 6.3 cm², while the second cube has an internal area of about 15.7 cm². The external surface area of both porous cubes is approximately 4.4 cm². This is the reason why the microporous materials have higher SSAs.

Figure 1-8: Two porous cubes of 1 cm³ with different pore sizes

The second reason for the greater adsorption that is achieved in micropores is the higher potential of adsorption that these pores have. The adsorption potential of a flat surface is a single potential well, as presented in Figure 1-9a. Then, when two or more surfaces are close to each other, such as inside a pore, an overlap of potentials between the opposite walls is produced, as Figure 1-9b shows. This overlap of potentials generates a stronger adsorption potential inside the pore (dashed line in Figure 1-9b), which increases the amount of hydrogen adsorbed. When the pores are narrower, the total adsorption potential produced by the overlap is greater. Figure 1-9c presents a comparison between the adsorption potentials of 0.65, 1.00, and 1.50 nm pores, and the narrower pore clearly has a greater potential for adsorption.
Figure 1-9: a) Potential energy diagram for adsorption in a flat surface (Toth et al., 2015), b) overlap of adsorption potentials inside a slit-shaped pore (Beckner & Dailly, 2014), and c) comparison of the adsorption potentials of 0.65, 1.00 and 1.50 nm pores (Knight et al., 2020)
1.2.2.3 Adsorbent density effect

Most studies about hydrogen storage on activated carbons or other adsorbents do not consider the volumetric storage density of hydrogen and only report the gravimetric storage density (i.e., wt%). The volumetric storage density is as important as the gravimetric storage density, and it may be even more important depending on the application. For example, Marinelli et al. (2020) analyzed the application of an intermetallic hydride (LaNi$_5$H$_6$) for a stationary storage of hydrogen. This intermetallic hydride has a reversible gravimetric capacity of 1.2 wt% and a volumetric capacity of 87.0 kg/m$^3$. Despite its low gravimetric capacity, its volumetric capacity exceeds the capacity of compressed or liquid hydrogen. This is due to the high density of the material (over 7000 kg/m$^3$), and because it was used in a stationary application, the weight of the intermetallic hydride was not a critical parameter.

The same phenomenon occurs on activated carbons and in other adsorbents. As presented in Figure 1-10, the density of activated carbons decreases as the SSA increases. Due to this decrease in density, there is an optimal SSA or micropore volume where the maximum volumetric adsorption capacity is reached. Figure 1-11 shows this effect. The dashed line represents the tendency of the hydrogen volumetric capacity of different activated carbons, and the continuous line represents their gravimetric capacity. As the micropore volume increases, the volumetric capacity increases until an inflection point, where it begins to decrease. And as explained before, the gravimetric capacity increases with the increment of the micropore volume. Then, to have a good performance for hydrogen storage using activated carbons or other adsorbents, a trade-off must be found between the micropore volume (or SSA) and the material's density (Lozano-Castelló et al., 2013).
Figure 1-10: Packing and tap density of powder activated carbons versus their SSA (Lozano-Castelló et al., 2013)

Figure 1-11: Hydrogen adsorption capacities of activated carbon samples at 77 K and 4 MPa versus micropore volume. Volumetric and gravimetric capacities are represented by the dashed and continuous lines, respectively (Lozano-Castelló et al., 2013)
1.2.2.4 Surface functional groups effect

Generally, activated carbons are loaded with functional groups, and their influence on hydrogen adsorption has been studied before. The functional groups are located at the edges of the graphitic basal planes of the carbonaceous materials (see Figure 1-12). There are different kinds of functional groups, which are classified as acidic (e.g., carboxylic, lactone, phenol, lactol), basic (e.g., chromene, ketones, pyrones), and neutral (Shafeeyan et al., 2010).

![Functional groups](image)

Figure 1-12: Acidic and basic surface functionalities located at the edges of a graphitic basal plane (Shafeeyan et al., 2010)

Despite all the studies that have been done, there are still contradictions about the effect of functional groups on hydrogen adsorption. On the one hand, some studies indicate that the presence of surface oxygen groups has negative effects on hydrogen adsorption, due to the reduction of the interactions between adsorbate and adsorbent, the saturation of the adsorption sites, and steric hindrance effects (obstruction of pore access) (Bleda-Martínez et al., 2008; Georgakis et al., 2007; Zhao et al., 2005).
Bleda-Martínez et al. (2008) showed that an activated carbon with a high content of surface oxygen groups adsorbed 38% less hydrogen than another activated carbon with similar SSA and low functional groups. Meanwhile, Huang et al. (2010) concluded that hydrogen adsorption on activated carbons at 77 K and RT is independent of the concentration of basic groups, and the presence of acidic groups above 0.8 mmol/g has a negative effect. On the other hand, Rossetti & Ramis (2013) determined that the hydrogen adsorption at 273 K improved between 73 and 150% with the oxidation of the activated carbon samples with hot air, despite the loss of 26 to 32% of SSA. This was attributed to an increment in the interaction between hydrogen and the adsorbent. Also, the oxidation caused a decrease of 46 to 57% in adsorption of hydrogen at 77 K due to the loss of SSA.

1.2.2.5 Doping effect

As mentioned earlier, the Van der Waals interactions implied in adsorption are relatively weak (lower than 10 kJ/mol), which is the reason for the low hydrogen storage densities and the requirement of low temperatures and high pressures for adsorption. To improve the hydrogen storage on activated carbons and in other carbon materials, the adsorption enthalpy should be between 20 and 30 kJ/mol (Boateng et al., 2020; Niaz et al., 2015; Sankaran & Viswanathan, 2006; Zhao et al., 2019). One way to increase the adsorption enthalpy of hydrogen is by adding external elements to the activated carbons (doping). There are different effects that dopants have on adsorbate/adsorbent interactions, such as the induction of Kubas interactions, the spillover effect, and electron density distortions (Boateng et al., 2020; Sankaran & Viswanathan, 2006; Yu et al., 2017). The three main dopant groups are transition metals (e.g., Pt, Pd, Ni, Cu, Rh), alkali and alkaline earth metals (e.g., Li, Na, Mg, Ca), and heteroatoms (e.g., N, B, P) (Geng et al., 2015; Rossetti et al., 2015).
For transition metals, there have been reported increments of hydrogen adsorptions in carbon materials of 100% with Pt (at RT and 100 bar), 29% with Pd (at RT and 60 bar), 228% with Ni (at RT and 100 bar) and 149% with Cu (at RT and 100 bar) (Huang et al., 2010; Rossetti et al., 2015; Stuckert et al., 2010). As far as the alkali metals are concerned, Challet et al. (2004) reported adsorptions of 1.73 wt% and 0.97 wt% (at RT and 30 bar) for Li and K doped activated carbons, respectively, but the adsorptions were irreversible due to the formation of stable alkali hydrides. Chen et al. (1999) produced carbon nanotubes (CNT) doped with Li and K, and hydrogen adsorptions were tested at ambient pressure in a range of temperatures between 300 and 800 K. The hydrogen uptakes were 20 wt% and 14 wt%, respectively, with adsorption/desorption cycles between the mentioned temperatures. In contrast with this study, Yang (2000) replicated the experimental procedure but used water traps to remove the moisture from the hydrogen before the adsorption process. The results showed adsorptions of 2.5 wt% and 1.8 wt% for Li and K doped CNT, respectively, and without the water trap, the results were similar to those presented by Chen et al. (1999). This effect is explained by the formation of alkali hydroxides and hydrates in the experiments with moisture in hydrogen.

There are many studies about doping carbon materials with nitrogen by different procedures, such as modifications with ammonia gas flow, ammonia solution, and urea (Giraudet & Zhu, 2011; Kang et al., 2009; Kopac & Kirca, 2020, Zhao et al., 2013; Zhao et al., 2019). Some of these studies show improvements in hydrogen adsorption. Kang et al. (2009) increased the adsorption of hydrogen on carbon xerogels at 77 K and 15 bar from 1.88 wt% to 3.24 wt%, and at RT, there was no considerable improvement; even in some samples, the adsorption decreased. The increment at 77 K can be attributed to the higher SSA of the doped samples (1602 m²/g) in contrast with the undoped ones (787 m²/g). Giraudet et al. (2011) presented an increment of adsorption going from 2.30 wt% to 2.80 wt% at 77 K on mesoporous carbons and from 0.12 wt% to 0.22 wt% at RT, both at 30 bar pressure. In this case,
there was an increment of 14% in SSA, but the increment in hydrogen adsorption was greater (22%). This shows that nitrogen has a contribution beyond the SSA modifications. Wang & Yang (2009) reported a nitrogen-doped microporous carbon with 18% higher hydrogen adsorption at RT compared with a pure carbon with a similar SSA. Finally, Zhao et al. (2013) decreased the adsorption of activated carbons that were doped with nitrogen due to the loss of SSA caused by the modification.

Boron is another heteroatom studied for doping carbon materials. Kopac et al. (2020) doped an activated carbon with an ammonia solution and then applied a solution of borax decahydrate at different concentrations at 40 °C for 2 h. The boron modification of the nitrogen-doped activated carbon improved the SSA from 2195 m²/g to 3037 and 2661 m²/g for the 0.075 and 0.1 M boron-doped samples. The hydrogen adsorptions were performed at 77 K and up to 1 bar. The undoped activated carbon reached hydrogen adsorption of 4.11 wt%, the nitrogen-doped sample reduced its capacity to 2.35 wt%, and the one doped with nitrogen and 0.075 M of boron had an improvement, reaching 4.14 wt%. Wang et al. (2009) synthesized a microporous carbon of 3771 m²/g from a zeolite template. The microporous carbon was mixed with boron oxide and heated at 1423 K for 1 h under an atmosphere of ammonia diluted in helium. This procedure reduced the SSA to 1215 m²/g, and the doped sample reached a hydrogen storage capacity of 0.55 wt% at 298 K and 100 bar. This capacity is 53% greater than the capacity of CMK-3 pure carbon (1260 m²/g of SSA). Ariharan et al. (2016) synthesized boron substituted carbon materials by the carbonization of resorcinol and triethyl borate at 600 and 800 °C under a nitrogen atmosphere. The samples had low SSAs of 23 y 65 m²/g with around 10 wt% of boron. The best sample reached 5.9 and 1.1 wt% of hydrogen adsorption at 298 and 77 K, respectively, under 100 bar pressure. In comparison, a similar sample without boron reached 0.22 and 0.18 wt% of hydrogen under the same conditions. Pfeifer et al. (2012) doped an activated carbon of 2500 m²/g with decaborane by
vapor deposition. The doping process reduced the SSA of the sample to 2100 m$^2$/g, but anyway, the doped sample adsorbed 20% more hydrogen than the undoped sample.

1.3 Working Hypothesis

Based on the literature review and personal judgment, it is believed that it is possible to improve the adsorption of hydrogen on activated carbons through a doping process with nitrogen and/or boron, and by the partial elimination of surface functionalities. Furthermore, it is important to consider that the improvement in adsorption is only possible if the modifications applied to the activated carbon do not generate a significant loss of SSA and micropore volume, because these parameters are relevant for the hydrogen adsorption.

1.4 Objectives

The main objective of this study was to develop a modification procedure for a commercial activated carbon to improve its hydrogen adsorption capacity at 77 K and up to 0.93 bar pressure. The specific objectives of this study were:

i) To study the effect of the modification of the surface organic groups, and of the doping with nitrogen and/or boron in activated carbons on the hydrogen adsorption capacity.

ii) Evaluate the effect of co-doping with nitrogen and boron on the hydrogen adsorption capacity of activated carbons.
iii) Correlate the physicochemical properties of activated carbons with their hydrogen adsorption capacity at 77 K and up to 0.93 bar.

iv) Estimate the hydrogen adsorption capacity of activated carbons at 77 K and up to 100 bar pressure by applying the Dubinin-Astakhov adsorption model.

Activated carbon was selected as hydrogen adsorbent due to its relatively low cost, high SSA, abundance in the market, and established industrial production. Nitrogen and boron were selected as dopants because they seem to improve hydrogen adsorption at 77 K and RT, not like transition metals or alkali and alkaline earth metals, which show poor performance at 77 K in some studies (Challet et al., 2004; Giraudet et al., 2011; Rossetti et al., 2015; Zhao et al., 2019). Another reason to use them is their abundance and lower cost compared with transition metals like platinum or palladium. In addition, there are different results about hydrogen adsorption on carbon materials doped with nitrogen and/or boron. Some authors presented decreases in hydrogen adsorption at 77 K caused by the doping of the adsorbents, while other authors had increments. Then, it is important to investigate those differences. Finally, there are not many experimental studies about hydrogen adsorption on activated carbons doped with boron, which makes it interesting to deepen that subject.
2. MATERIALS AND METHODS

2.1 Activated Carbon Samples

For the development of this study, the different activated carbon samples were supplied by Haycarb USA Inc. (USA), Medibro Corporation Limited (China), Lvyuan Water Treatment Technology Co. (China), Nicolaides S.A. (Chile), and the University of Tarapacá (Chile). The materials supplied by these entities were coconut shell based activated carbons, coal based activated carbons, and biochars (pyrolyzed biomass).

After the measurement of SSA and hydrogen adsorption of the different carbons, the sample supplied by Haycarb USA Inc. was selected as the main activated carbon sample for this study. Then, the modification procedures were applied to this activated carbon. It was selected because it has the highest SSA and the greatest hydrogen adsorption capacity among the samples. It is a granular activated carbon manufactured from coconut shell charcoal, and it has a mesh size of 4x18 (4.75 mm x 1 mm). Although only one activated carbon was selected for the modifications, the results and characterizations obtained with the other carbons are presented in the APPENDIX section.

2.2 Sample Preparation

The supplied activated carbon sample was designated AC, and different modification processes were applied to it, which are described below.
2.2.1 Functional groups modification

The functional groups of the AC sample were modified by a heat treatment under a He flow in a tubular furnace. The temperatures were held at 200 and 400 °C for 1 h with a 100 cm³/min STP flow rate, generating two different samples. The obtained samples were designated AC-He200 and AC-He400, respectively. With these treatment temperatures, the elimination of carboxylic and lactone groups was expected (Shafeeyan et al., 2010). The temperatures were not higher than 400 °C to avoid the total decomposition of the activated carbon.

2.2.2 Ammonia modification

Anhydrous ammonia with 99.5% of concentration was supplied by Nittra S.A. The modifications of the samples were carried out at a fixed temperature in a tubular furnace where the NH₃ flowed for 3 h with a flow rate of 50 cm³/min STP. In the first place, the AC and AC-He400 samples were modified at a fixed temperature of 500 °C. The resulting samples were designated AC-N500 and AC-He400-N500, respectively. These two samples were produced to determine if the presence of functional groups influences the NH₃ doping and posterior hydrogen adsorption. In the second place, the AC-He400 sample was modified with NH₃ at 400 and 600 °C, generating the AC-He400-N400 and AC-He400-N600 samples.
2.2.3 Boron modification

Borax decahydrate with 99.50% min. equivalent of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was supplied by Sigma-Aldrich. The activated carbon samples were doped through an incipient wetness impregnation technique, using demineralized water as solvent. The amount of borax decahydrate added to the solution was calculated to obtain a 5 wt% of boron on the activated carbon. After the impregnation, the samples were kept at RT for 8 h, and finally, they were dried at 80 °C. The AC and AC-He400 samples were modified with this procedure, producing the AC-B and AC-He400-B samples. Also, the AC-B and AC-He400-B samples were treated with helium at 400 °C for 1 h, to clear the pores and decompose the borax decahydrate molecule, producing the AC-B-He400 and AC-He400-B-He400 samples.

2.2.4 Nitrogen and boron modification

Activated carbon samples co-doped with nitrogen and boron were produced following the doping procedures presented above. The AC-He400-B sample was treated with $\text{NH}_3$ for 3 h at 500 °C, generating the AC-He400-B-N500 sample. The AC-He400-N500 sample was impregnated with 5 wt% of boron, yielding the AC-He400-N500-B sample.
2.3 Characterization of Activated Carbons and Hydrogen Storage

There are numerous methodologies to characterize activated carbons and other porous materials. These methods can provide information about the structure, adsorption capacity, surface functionalities, acidity and basicity of the surface, thermal stability, among others. The characterization methods used in this study are described below.

2.3.1 Nitrogen adsorption/desorption isotherms

2.3.1.1 Theoretical foundation

One of the most important characterization methods is the adsorption and desorption of nitrogen. This method consists of constructing the isotherms of adsorption and desorption with an automatic adsorption analyzer and using nitrogen as adsorbate. A lot of information can be obtained from nitrogen adsorption/desorption isotherms, such as the porous structure of the material, its specific surface area, pore volumes, and pore size distribution.

The isotherms are constructed at liquid nitrogen temperature (77 K) and in a relative pressure range of 0–1 \( \frac{p}{p^0} \), where \( p^0 \) is the saturation pressure of nitrogen at 77 K. The most used method for the construction of the isotherms is the gas adsorption manometry. This method is based on the change of pressures in a fixed and known volume. When the adsorption occurs, the pressure of the system drops until the equilibrium state is reached. This pressure variation is measured and then translated into an amount of nitrogen adsorbed. The most common technique is to measure the adsorption by increasing the pressure step by step until reaching the nitrogen saturation pressure and then reducing the pressure in the same way to build the
desorption isotherm. At each step, the equilibrium state is reached before moving on to the next step. Therefore, the whole process can take more than 10 h. Prior to the construction of the nitrogen isotherm, the free volume of the system with the sample inside (dead space) is measured by adsorption of helium, and a vacuum outgassing process is carried out to remove physisorbed molecules (Sing, 2001). This procedure is explained in more details by Thommes et al. (2015):

A static manometric determination entails the measurement of changes of pressure of calibrated gas volumes: a known amount of pure gas is admitted to a confined, calibrated volume containing the adsorbent, which is maintained at constant temperature. As adsorption takes place, the pressure in the confined volume falls until equilibrium is established. The amount of gas adsorbed at the equilibrium pressure is given as the difference between the amount of gas admitted and the amount of gas required to fill the space around the adsorbent, i.e., the dead space. The adsorption isotherm is usually constructed point-by-point by admission of successive charges of gas to the adsorbent with the aid of a dosing technique and application of the appropriate gas laws. The volume of the dead space must, of course, be known accurately: it is obtained either by pre-calibration of the confined volume and subtracting the volume of the adsorbent (calculated from its density or by the admission of a gas which is adsorbed to a negligible extent). (p. 1055-1056).

a) Porous structure of the material

The porous structure of activated carbons or other porous materials can be roughly determined based on the shape of their nitrogen adsorption/desorption isotherms. Depending on the shape of the curves, isotherms are classified into different types. Originally there are six types of isotherms, which were established by the International Union of Pure and Applied Chemistry (IUPAC), but this classification can be refined to eight types as shown in Figure 2-1 (Thommes et al., 2015).
Type I isotherms correspond to microporous materials. There is an upper limit for the adsorption that depends mainly on the accessible micropore volume. “A steep uptake at very low $p/p^0$ is due to enhanced adsorbent-adsorptive interactions in narrow micropores (micropores of molecular dimensions), resulting in micropore filling at very low $p/p^0$” (Thommes et al., 2015, p. 1059). Based on this, Type I(a) isotherms correspond to microporous materials with mainly narrow micropores (< 1 nm), while Type I(b) isotherms are given by microporous materials that also have wider micropores and possibly narrow mesopores (< 2.5 nm).
Type II isotherms are given by the adsorption on nonporous or macroporous adsorbents. A sharp knee (Point B) corresponds to the completion of the monolayer coverage, while a more gradual curvature shows an overlap between the monolayer and multilayer coverages.

Type III isotherms are related to nonporous or macroporous adsorbents with weak adsorbent-adsorbate interactions.

Type IV isotherms are associated with mesoporous materials, there is an initial adsorption in the mesopores followed by a pore condensation at higher relative pressures, reaching a final saturation plateau before the saturation pressure \((p/p_0=1)\). The Type IV(a) isotherm shows a hysteresis cycle, which appears when there are mesopores wider than 4 nm, while the Type IV(b) isotherm is associated with adsorbents with smaller mesopores.

Type V isotherms are related to materials with weak adsorbent–adsorbate interactions at low pressures, and the pore filling starts at higher pressures. “Type V isotherms are observed for water adsorption on hydrophobic microporous and mesoporous adsorbents” (Thommes et al., 2015, p. 1059).

Finally, Type VI isotherms are given by a layer-by-layer adsorption on materials with a uniform and nonporous surface (Thommes et al., 2015).

More information about the pore structure can be obtained from the hysteresis cycles. Hysteresis is associated with capillary condensation and metastability in the adsorption/desorption process. In more detail:
the desorption path is often dependent on network effects and various forms of pore blocking. These phenomena occur if wide pores have access to the external surface only through narrow necks (e.g., ink-bottle pore shape). The wide pores are filled as before and remain filled during desorption until the narrow necks empty at lower vapour pressures. In a pore network, the desorption vapour pressures are dependent on the size and spatial distribution of the necks. If the neck diameters are not too small, the network may empty at a relative pressure corresponding to a characteristic percolation threshold. (Thommes et al., 2015, p. 1060).

There are different types of hysteresis loops and their classifications are presented in Figure 2-2.

![Figure 2-2: Classification of hysteresis loops (Thommes et al., 2015)](image)

Type H1 hysteresis loops are related to materials with a narrow range of uniform mesopores (e.g., templated silicas, controlled pore glasses, and ordered mesoporous carbons).
About Type H2 loops, the “very steep desorption branch, which is a characteristic feature of H2(a) loops, can be attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation” (Thommes et al., 2015, p. 1061), while the Type H2(b) loop is associated with a larger size distribution of neck widths. H2(a) loops can be found in silica gels, some porous glasses, and in some ordered mesoporous materials, while H2(b) loops “have been observed with mesocellular silica foams and certain mesoporous ordered silicas after hydrothermal treatment” (Thommes et al., 2015, p. 1061).

Type H3 hysteresis loops “are given by non-rigid aggregates of plate-like particles (e.g., certain clays) but also if the pore network consists of macropores which are not completely filled with pore condensate” (Thommes et al., 2015, p. 1061).

The adsorption branch of Type H4 loops is a composite of Type I and II isotherms. There is a high uptake at low relative pressures, which is associated with the micropore filling. H4 loops can be found in micro-mesoporous carbons, aggregated crystals of zeolites, and some mesoporous zeolites.

Finally, Type H5 loops are unusual, and their form is “associated with certain pore structures containing both open and partially blocked mesopores (e.g., plugged hexagonal templated silicas)” (Thommes et al., 2015, p. 1061).

b) Specific surface area

The specific surface area (SSA) is the total surface area that materials have per unit of mass. The specific surface area consists almost entirely of the inner surface of the pores, with a negligible contribution from the outer surface of the material. The SSA shows a direct relationship with the porosity of a material, and it is one of the most used parameters to compare the porous development of materials. The measurement of the SSA is based on the monolayer capacity, which is defined as the amount of
adsorbate required to cover the entire surface of the material with a monolayer of molecules (Thommes et al., 2015). The SSA is calculated based on the equation expressed below:

\[
SSA = n_m \cdot L \cdot \sigma_m
\]  \hspace{1cm} (2.1)

In Equation 2.1 \(n_m\) is the monolayer capacity expressed in moles of adsorbate per gram of adsorbent (mol/g), \(L\) is the Avogadro's constant \(\left(6.022 \cdot 10^{23} \text{ mol}^{-1}\right)\), and \(\sigma_m\) is the area that an adsorbed molecule occupies on the surface of the adsorbent (molecular cross-sectional area) expressed in nm\(^2\)/molecule. The molecular cross-sectional area of nitrogen at 77 K is 0.162 nm\(^2\)/molecule. Since \(L\) and \(\sigma_m\) are known values, it only remains to determine \(n_m\). The monolayer capacity \((n_m)\) is obtained from the nitrogen adsorption isotherm, and the most used method for this purpose is the application of the Brunauer–Emmett–Teller (BET) adsorption model (Thommes et al., 2015). The BET equation is expressed below:

\[
\frac{p/p^0}{n(1-p/p^0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}(\frac{p}{p^0})
\]  \hspace{1cm} (2.2)

In Equation 2.2, \(C\) is a positive parameter that is related to the monolayer adsorption energy, \(n_m\) is the monolayer capacity, and \(n\) is the amount adsorbed at a given pressure and it is expressed in mol/g (Thommes et al., 2015). To obtain the BET monolayer capacity there are two possible procedures.

The first procedure, which is the original procedure, consists of plotting the BET equation using the nitrogen adsorption isotherm data, then establishing a linear fitting inside the 0.05-0.30 \(p/p^0\) range, and finally, the linear fitting is used to determine \(n_m\). To construct the BET plot, the expression \((p/p^0)/(n(1 - p/p^0))\) must be graphed versus \(p/p^0\) as shown in Figure 2-3. After applying the linear fitting to the BET plot, the monolayer capacity is calculated based on the intercept \((I)\) and the
slope \((m)\) of the linear regression. Two equations are required to establish the system:

\[
I = \frac{1}{n_mC} \quad (2.3)
\]

\[
m = \frac{c-1}{n_mC} \quad (2.4)
\]

And the solution of the system is:

\[
n_m = \frac{1}{I+m} \quad (2.5)
\]

Now with the BET monolayer capacity, the SSA of the sample can be calculated with Equation 2.1. Even though this methodology is the original procedure, the applied linear regression is arbitrary. Due to this arbitrariness, another procedure was developed, the so-called Rouquerol method. This method is a simplification of the BET model, which assumes that the parameter \(C\) for the adsorption of nitrogen in solids is large enough \((C > 100)\) to simplify the BET equation to the following one:

\[
n_{\text{Rouquerol}} = n(1 - p/p^0) \quad (2.6)
\]

Using Equation 2.6 the monolayer capacity can be found at the maximum of the Rouquerol plot \((n_{\text{Rouquerol}}\) versus \(p/p^0\)) (Sing et al., 1985). This function is concave, so the maximum is easily found, and again the SSA of the sample can be obtained with Equation 2.1. The Rouquerol method is widely accepted by researchers who work with porous materials because of its simplicity and impartiality.

The following figures show an example of the application of both procedures to obtain the BET SSA of a mesoporous material. Figure 2-3 shows the linear
regression of the BET plot at $0.05 < p/p^0 < 0.30$, and its respective SSA is 206 m$^2$/g. In this example, the linear regression was established between 0.05 and 0.30 $p/p^0$, but in other cases, the range could be another that is within the 0.05-0.30 $p/p^0$ range.

In Figure 2-4 the Rouquerol plot is presented, and the respective SSA is 201 m$^2$/g. Both SSAs are similar, and their difference is lower than 3%. Anyway, regardless of the procedure to be used, the application of the BET model to determine the SSA has an error of around 10%.

![BET Plot](image1)

**Figure 2-3**: BET plot with a linear regression at $0.05 < p/p^0 < 0.30$

![Rouquerol Plot](image2)

**Figure 2-4**: Rouquerol plot with its maximum value at 0.00206 mol/g
c) Pore volumes

As said before, microporous materials such as activated carbons have a negligible macropore volume, then the micro, meso, and total pore volumes are the volumes that are important to measure.

The micropore volume of a sample can be assessed applying the Dubinin Radushkevich equation:

\[
\log(n) = \log(n_0) - D \cdot \log^2(p^0/p) \quad (2.7)
\]

In Equation 2.7 \( n \) is the amount of nitrogen adsorbed, \( n_0 \) is the amount of nitrogen adsorbed into the micropores, and \( D \) is a constant that depends on the material (Sobolik et al. 1992). To determine \( n_0 \), Equation 2.7 must be plotted as \( \log(n) \) versus \( \log^2(P_0/P) \) using the nitrogen adsorption data. Then, a linear regression must be fitted in the range \( 1 < \log^2(P_0/P) < 2 \), and finally the intercept of the regression is equal to \( \log(n_0) \). An example of the Dubinin Radushkevich plot of an activated carbon is presented in Figure 2-5.

![Figure 2-5: Dubinin Radushkevich plot of an activated carbon with the respective linear regression](image)
Generally, the amount of nitrogen adsorbed \((n\) and \(n_0\)) is expressed in mol/g or cm\(^3\) STP/g, then the micropore volume is calculated from \(n_0\) considering the molar mass of nitrogen, its density at 77 K, and the molar volume at STP. In the example presented in Figure 2-5, \(n_0\) has a value of 421 cm\(^3\) STP/g, which is equivalent to 0.65 cm\(^3\)/g.

The mesopore volume of a sample is obtained as the difference between the total pore volume and the micropore volume. Then, it only remains to determine the total pore volume. The total pore volume is obtained from the amount of nitrogen adsorbed in the range of 0.95 – 1.00 \(p/p^\circ\). The activated carbon used in the last example adsorbs 439 cm\(^3\) STP/g of nitrogen at 0.99 \(p/p^\circ\). Then, the total pore volume corresponds to 0.68 cm\(^3\)/g and the mesopore volume to 0.03 cm\(^3\)/g.

d) Pore size distribution

The pore size distribution of a porous material represents the abundance of the different pore sizes (widths) that a sample has. The pore size distribution can be assessed in the microporous and mesoporous regions by applying different methodologies.

The micropore size distribution can be assessed by applying the Horvath-Kawazoe model (HK) or the non-local density functional theory (NLDFT) model. The HK model is based on molecular interactions, while the NLDFT model considers quantum mechanical equations. These models are complex, and they are included in the modern adsorption analyzers. The HK model is more used than the NLDFT because a template is required to apply the NLDFT model, which is different for each material and is not always available.

The mesopore size distribution can be determined by applying the NLDFT model or the Barrett, Joyner, Halenda (BJH) method. The BJH method is based on the
Kelvin model of pore filling and is constructed using the nitrogen desorption isotherm. The pore diameter is calculated as:

\[ w = 2 \cdot (r_k + t) \quad (2.8) \]

Where \( w \) is the pore diameter, \( r_k \) is the Kelvin radius, and \( t \) is the monolayer thickness. The Kelvin radius expressed in nm can be obtained from:

\[ r_k = -0.414/\log (p/p^0) \quad (2.9) \]

And the monolayer thickness expressed in nm can be calculated from the Halsey equation:

\[ t = 0.354 \cdot (-5/\ln (p/p^0))^{1/3} \quad (2.10) \]

Then, Equation 2.8 gives different widths at different relative pressures, and the volume of nitrogen adsorbed also varies with the pressure. Finally, the relative abundance of the different pore widths is calculated as the fraction between the adsorbed volume differentials (dV) and the pore width differentials (dw). This information is presented in a plot of dV/dw versus pore width as shown in Figure 2-6.
Figure 2-6: BJH pore size distribution of a mesoporous material

2.3.1.2 Experimental methodology

Nitrogen adsorption/desorption isotherms were constructed using a Micromeritics® 3Flex adsorption analyzer (Figure 2-7a). Prior to the adsorption process, the samples were degassed under vacuum for 4 h at 300 °C using a Micromeritics® Smart VacPrep gas adsorption sample preparation device (Figure 2-7b). Then, the samples were placed in the 3Flex, and the void volume was determined with He before the start of nitrogen adsorption. During the adsorption process, the sample holder was immersed in liquid nitrogen to maintain the temperature at 77 K.
2.3.2 Temperature-programmed decomposition

2.3.2.1 Theoretical foundation

Temperature-programmed decomposition (TPD) analysis is used to determine the surface functional groups that are present in a sample. This analysis consists of heating the sample under an inert atmosphere, which causes the decomposition of the surface functionalities. Generally, the decomposition process generates emissions of CO and CO$_2$, and the decomposition of each kind of functional group occurs in a specific temperature range and is related to specific emissions as Figure 2-8 shows. In addition, the decomposition of carboxylic and phenolic groups is associated with the emission of H$_2$O. The heating of the sample occurs at a fixed heating rate, and the temperature range is from RT to 1000 °C. The amount and type
of emissions are determined by a thermal conductivity detector (TCD) and a mass spectrometer.

![Diagram of oxygenated functional groups on carbon with their respective decomposition temperatures and emissions](image)

**Figure 2-8:** Oxygenated functional groups on carbon with their respective decomposition temperatures and emissions (Shafeeyan *et al.*, 2010)

### 2.3.2.2 Experimental methodology

The temperature-programmed decomposition (TPD) analyses were performed in the Micromeritics® 3Flex apparatus equipped with a TCD and connected to an MKS Cirrus 2 mass spectrometer (Figure 2-9). The analyses were carried out under a flow of He with a heating rate of 10 °C/min, starting at RT and ending at 1000 °C. These TPD analyses gave information about CO, CO₂, and H₂O emissions produced by the decomposition of the AC, AC-He200, and AC-He400 samples. The as-received data were expressed in arbitrary units (a.u.) versus temperature, and they were
normalized by the mass and the SSA of the respective samples. Then, the results are presented in a.u./m$^2$ versus °C.

![MKS Cirrus 2 mass spectrometer](https://www.ccrprocessproducts.com/)

Figure 2-9: MKS Cirrus 2 mass spectrometer (Source: https://www.ccrprocessproducts.com/)

### 2.3.3 X-ray photoelectron spectroscopy

#### 2.3.3.1 Theoretical foundation

X-ray photoelectron spectroscopy (XPS) is a technique used to analyze the composition of the surface of solid materials (0.5 to 3 nm beneath the surface). This technique relies on the photoelectric effect and provides information about the elements present in the material, their oxidation states, their relative abundance, and their chemical environment. The main components of an XPS analyzer are the X-ray source, which produces the X-ray beam; the analysis chamber, where the sample is placed under vacuum; the energy analyzer, which measures the kinetic energy of electrons; the electron detector, which counts the emitted electrons; and the electron optics, which directs the electrons to the energy analyzer and electron detector. When the X-ray beam reaches the surface of the material, electrons are emitted as the atoms ionize, then these electrons pass through the energy analyzer to finally
reach the electron detector. Applying the equation of the photoelectric effect, the binding energy can be determined:

\[ E_K = h \cdot v - E_B - \phi_{sp} \]  \hspace{1cm} (2.11)

In Equation 2.11 \( E_K \) is the kinetic energy of the emitted electron, \( h \cdot v \) is the energy of the X-ray photon, \( E_B \) is the binding energy of the electron, and \( \phi_{sp} \) is the work function of the spectrometer. Then, the data obtained from an XPS analysis is presented as the electron count rate versus the binding energy in eV. Figure 2-10 shows the XPS spectrum of a boron substituted carbon material. Figure 2-10a shows the complete XPS spectrum, while Figure 2-10b shows the deconvolution of the B 1s peak.

Figure 2-10: X-ray photoelectron spectroscopy of a boron substituted carbon material a) XPS-Survey spectrum and b) B 1s (Ariharan et al., 2016)

The relative abundance of an element can be assessed based on the area under the peaks:
\[ C_x = \frac{I_x/S_x}{\sum_i I_i/S_i} \]  

(2.12)

In Equation 2.12, \( C_x \) is the atomic concentration of the element \( x \), \( I_x \) is the intensity of the peak associated with the element \( x \) (which is calculated as the area under the peak), \( I_i \) is the intensity of the peak associated with the \( i \)-th element, \( S_x \) is the atomic sensitivity factor of the element \( x \), and \( S_i \) is the atomic sensitivity factor of the \( i \)-th element.

2.3.3.2 Experimental methodology

The XPS spectra of the AC, AC-He400, AC-N500, AC-He400-N500, AC-B, AC-B-He400, and AC-He400-B-He400 samples were performed using a SPECS GmbH with UHV system and with an energy analyzer PHOIBOS 150 9MCD. A non-monochromatic Mg K\( \alpha \) X-ray source (1253.6 eV) was used for the analysis. The C 1s peak (284.6 eV) was used as a reference to measure the binding energies (BE), which were determined with an error of less than 0.01 eV. Shirley backgrounds and mixed Lorentzian-Gaussian functions were applied for the deconvolution of the data.

The positions of the peaks, which are used to identify the different chemical species, for the N 1s, B 1s, and O 1s spectra were determined based on a literature review. The chemical species and their binding energies considered for the N 1s spectrum are pyridine at \( \approx 398.5 \) eV, pyridone and pyrrole at \( \approx 400.5 \) eV, quaternary nitrogen at \( \approx 401.2 \) eV, and oxidized nitrogen at \( \approx 402.9 \) eV (Kang et al., 2009). For the B 1s spectrum, the species that were taken into account are BCO\(_2\) at \( \approx 192.5 \) eV and B–O at \( \approx 193.3 \) eV (Balaji et al., 2019). The BCO\(_2\) species corresponds to boron bonded with carbon and oxygen (\( i.e. \), boron is incorporated into the carbon matrix), and the B–O species is associated with boron bonded only with oxygen (\( i.e. \), Na\(_2\)B\(_4\)O\(_7\) or B\(_2\)O\(_3\)). Finally, the species considered for the O 1s spectrum are anhydride/lactone.
groups (O–C=O) at \( \approx 531.3 \) eV, quinone/carbonyl groups (C=O) at \( \approx 532.3 \) eV, ether/phenolic groups (C–O–) at \( \approx 533.5 \) eV, carboxylic groups (COOH) at \( \approx 534.3 \) eV, and chemisorbed water or oxygen at \( \approx 536.2 \) eV (Li et al., 2019; Li et al., 2020).

![Diagram of nitrogen functionalities in nitrogen-doped carbon materials with their respective XPS peak positions](image)

Figure 2-11: Nitrogen functionalities in nitrogen-doped carbon materials with their respective XPS peak positions (Kang et al., 2009)

### 2.3.4 Density-functional theory

#### 2.3.4.1 Theoretical foundation

Density-functional theory (DFT) is a computational quantum mechanical method used in chemistry, physics, materials science, and engineering to model chemical systems and calculate their structures and properties (Lipkowitz & Boyd, 1996; Blinder, 2021). This method is based on the total electronic charge density, which is related to the wave function of a system, and it is “equivalent to solving Schrödinger’s equation and is, therefore, an exact theory for describing the electronic structure and properties of matter” (Lipkowitz et al., 1996, p.187).
2.3.4.2 Experimental methodology

To analyze the effect of the nitrogen functionalities on hydrogen adsorption, an activated carbon layer (ACL) was modeled, adding several nitrogen-containing functional groups, following the schematic model described by Moumaneix et al. (2020). Boundary atoms were capped with H atoms to keep properly charge stability.

ACL and H$_2$ were first optimized individually and then used to build the H$_2$-ACL complex models, where a pre-adsorbed H$_2$ was placed over the ACL with a distance of 2.75 Å between the H$_2$ molecule and the ACL. The adsorption sites are represented in Figure 2-12 (labeled from A to L). In the case of the L complex, the pyrrolic group at the A site was protonated to form a pyrrole group. Furthermore, since it was possible to identify several adsorption modes in the same defined region, X1 and X2 modes were established, being X the letters from A to L, respectively. Thus, a total of 15 complexes schematized in Figure 2-13 were studied. The complexes display the H$_2$ onto the bridge sites, i.e., over and along the C–C, C–N, N–O, and C–O bonds, except the E site, in which H$_2$ was placed over the hole.

![Figure 2-12: General scheme of the activated carbon layer and the H$_2$ adsorption sites labeled from A to L](image)
Figure 2-13: Scheme of the 15 initial positions of H$_2$ adsorption evaluated over the activated carbon layer

All complexes were evaluated by calculating their adsorption energies (defined in Equation 2.13) and the shortest interatomic distances between H$_2$ and the ACL. The adsorption energies ($E_{ads}$) were calculated considering:

$$E_{ads} = E_{(ACL+H_2)} - E_{(H_2)} - E_{(ACL)} \quad (2.13)$$

Where $E_{(ACL+H_2)}$ is defined as the complex energy formed by the ACL and the hydrogen molecule, while $E_{(H_2)}$ and $E_{(ACL)}$ are the molecular energies of the isolated H$_2$ and ACL species, respectively.

The geometry optimizations were calculated using B3LYP (Becke, 1988; Lee et al., 1988) and def2-SVP basis set as a pre-optimization step, followed by def2-TZVP basis set to improve the accuracy (Weigend & Ahlrichs, 2005). To obtain an accurate description of dispersion effects, empirical Grimme-D3 with Becke-Johnsson damping corrections were also included (Grimme et al., 2011). All calculations were
2.3.5 Hydrogen storage

2.3.5.1 Theoretical foundation

Hydrogen adsorption is evaluated by constructing the adsorption isotherm. This is done with the same methodology used for the construction of the nitrogen adsorption isotherms. As presented above, there are different models that describe the adsorption isotherm with mathematical equations. The equation of the Langmuir model (monolayer adsorption) is:

\[ q_e = \frac{Q_0 b C_e}{1 + b C_e} \]  \hspace{1cm} (2.14)

Where \( q_e \) is the amount of adsorbate in the adsorbent at equilibrium, \( Q_0 \) is the maximum monolayer coverage capacity, \( b \) is the Langmuir isotherm constant, and \( C_e \) is the equilibrium concentration (Foo et al., 2010). The equation of the Freundlich model (multilayer adsorption) is:

\[ q_e = K_F C_e^{1/n_F} \]  \hspace{1cm} (2.15)

Where \( K_F \) is the Freundlich isotherm constant, which is related to the adsorption capacity, and \( n_F \) is the adsorption intensity (Foo et al., 2010). As said before, the Redlich–Peterson (R-P) adsorption isotherm model is related to the Langmuir and Freundlich models and is expressed by an empirical equation with 3 parameters:

\[ q_e = \frac{K_R C_e}{1 + a_R C_e^p} \]  \hspace{1cm} (2.16)
Where $K_R$ is the Redlich–Peterson isotherm constant, $a_R$ is another isotherm constant and $g$ is the Redlich–Peterson isotherm exponent (Foo et al., 2010). When $1/K_R = 0$ the R-P equation becomes the same as the Freundlich isotherm equation, and when $g = 1$ the R-P equation is the same as the Langmuir isotherm equation (Wu et al., 2010). In addition, the fraction $K_R/a_R$ is related to the maximum monolayer coverage capacity (Belhachemi & Addoun, 2011; Wu et al., 2010).

Another relevant model to consider is the modified Dubinin-Astakhov (MDA) adsorption model. The MDA model was proposed by Richard et al. (2009), and it is suitable for modeling adsorption isotherms of gases in a supercritical state, then it can be applied to the adsorption of hydrogen at 77 K. The MDA equation for the excess adsorption is presented below:

$$n_{ex} = n_{max} \exp[(RT/\varepsilon)^m \ln^n(P_0/P)] - \rho_g V_a \quad (2.17)$$

Where $n_{max}$ is the limiting adsorption, $P_0$ is the pseudo-saturation pressure, $P$ is the pressure, $T$ is the temperature; $R$ is the universal gas constant (8.314 J/(mol K)), $\varepsilon = \alpha + \beta T$ is the characteristic free energy of adsorption, where $\alpha$ is the enthalpic factor and $\beta$ is the entropic factor, $m$ is a distribution parameter (generally around 2 for activated carbons), $V_a$ is the adsorption volume, and $\rho_g$ is the gas phase density (Richard et al., 2009).

When hydrogen is stored inside a tank filled with an adsorbent, it is stored by adsorption and compression. Adsorption occurs within the adsorption volume ($V_a$), while compression occurs out of the adsorption volume ($V_{free}$). Then, there are two phases with different densities, the adsorbed and the gas phases. The sum of $V_a$ and $V_{free}$ gives the total void volume of the adsorption system ($V_{v,sys}$), which includes the pore volume, the interstitial space, and any additional empty space. Generally, $V_{v,sys}$ is measured by helium probing and $V_a$ cannot be measured directly (Richard
et al., 2009). Since the adsorption of gases is measured as excess adsorption, which is the difference between the total amount of gas stored (adsorbed and compressed) at a given pressure and temperature, and the amount that would be stored just by compression in the same volume \( V_{v,sys} \) at the same pressure and temperature, it is important to use an adsorption model for excess adsorption to model the experimental data.

Another parameter that is important to consider when hydrogen is stored inside a tank filled with an adsorbent is the volumetric hydrogen storage density. To calculate this value, Lozano-Castelló et al. (2013) defined the following equation for a tank filled with an adsorbent:

\[
    n_S = n_{ex} + \rho_g (1 - \rho_a/\rho_{He})
\]  

(2.18)

Where \( n_S \) is the total amount of hydrogen stored in a tank (on a volumetric basis), \( n_{ex} \) is the excess hydrogen adsorption (on a volumetric basis), \( \rho_g \) is the gas phase density, \( \rho_a \) is the bulk density, and \( \rho_{He} \) is the skeletal or helium density. The bulk density is defined as the mass of the adsorbent divided by the total volume that it occupies inside a container, and the skeletal density corresponds to the density of the carbonaceous structure. In Equation 2.18 the right term \( \rho_g (1 - \rho_a/\rho_{He}) \) corresponds to the hydrogen that is stored by compression, then if the excess adsorption is added to it, the total amount of hydrogen stored is obtained. Considering the bulk density of the adsorbent, the total amount stored can be expressed on a volumetric or gravimetric basis.

2.3.5.2 Experimental methodology

Hydrogen adsorption was performed in the same Micromeritics\textsuperscript{®} 3Flex apparatus with the previous degasification of the system. The pressure range for the adsorption
was from 0 to 0.93 bar, the temperature was set at 77 K with liquid nitrogen, and the adsorption time was between 5 and 9 h, depending on the sample. The adsorption was measured in weight percent (wt%), which is considered in this study as the fraction between the mass of the hydrogen adsorbed and the mass of the adsorbent.

In addition, the modified Dubinin-Astakhov (MDA) adsorption model was fitted with experimental data of the sample that had the best hydrogen adsorption performance, and it was used to extrapolate the adsorption up to 100 bar pressure. The parameters $n_{max}$, $P_0$, $\alpha$, $\beta$, $m$, and $V_a$ were determined by fitting the MDA model with the experimental data using Microsoft Excel. To fit the model, the gas phase densities ($\rho_g$) were determined for the different pressures using Aspen Plus V12.1 with REFPROP (NIST Reference Fluid Thermodynamic and Transport Properties Database).

After the MDA model was fitted and the adsorption was modeled up to 100 bar pressure, the hydrogen storage density of a tank filled with the activated carbon was evaluated using Equation 2.18. The bulk density ($\rho_a$) was calculated by placing a certain mass of activated carbon inside a graduated cylinder and measuring the volume it occupies, and the skeletal density ($\rho_{He}$) was measured by helium pycnometry in the Micromeritics 3Flex.
3. RESULTS AND DISCUSSION

3.1 Nitrogen Adsorption/Desorption Isotherms

The N$_2$ adsorption isotherms of the different samples are presented in Figure 3-1. They can be classified as Type I(b) isotherms according to the IUPAC classification, which is associated with materials with a wide distribution of micropores and with a little contribution of narrow mesopores. The hysteresis cycle is classified as H4, which is related to materials with complex structures such as activated carbons that have micro and mesopores (Thommes et al., 2015).

![Figure 3-1: N$_2$ adsorption/desorption isotherms of the a) original (AC) and heat-treated samples, b) ammonia-treated samples, c) boron-treated samples, and d) ammonia/boron-treated samples](image-url)
All isotherms have a similar shape, but they differ in the slope at low pressures and in the final amount adsorbed. This leads to different specific surface areas and pore volumes. Table III-1 summarizes the SSAs and pore volumes of the samples. The mesopore volume \( V_m \) contributes between 0.00 and 4.26% of the total pore volume of the different samples, which agrees with the IUPAC classification and shows that the ratio of mesopores to micropores remains almost the same despite the modifications.

Table III-1: Textural characteristics of the different activated carbon samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>SSA(^a) ((\text{m}^2/\text{g}))</th>
<th>( V_0 )^(b) ((\text{cm}^3/\text{g}))</th>
<th>( V_m )^(c) ((\text{cm}^3/\text{g}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1678</td>
<td>0.70</td>
<td>0.03</td>
</tr>
<tr>
<td>AC-He200</td>
<td>1512</td>
<td>0.63</td>
<td>0.01</td>
</tr>
<tr>
<td>AC-He400</td>
<td>1572</td>
<td>0.66</td>
<td>0.01</td>
</tr>
<tr>
<td>AC-N500</td>
<td>1646</td>
<td>0.70</td>
<td>0.02</td>
</tr>
<tr>
<td>AC-He400-N400</td>
<td>1554</td>
<td>0.64</td>
<td>0.02</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>1554</td>
<td>0.65</td>
<td>0.02</td>
</tr>
<tr>
<td>AC-He400-N600</td>
<td>1514</td>
<td>0.64</td>
<td>0.01</td>
</tr>
<tr>
<td>AC-B</td>
<td>1407</td>
<td>0.57</td>
<td>0.02</td>
</tr>
<tr>
<td>AC-B-He400</td>
<td>1100</td>
<td>0.45</td>
<td>0.01</td>
</tr>
<tr>
<td>AC-He400-B</td>
<td>1047</td>
<td>0.43</td>
<td>0.01</td>
</tr>
<tr>
<td>AC-He400-B-He400</td>
<td>1003</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>AC-He400-B-N500</td>
<td>853</td>
<td>0.35</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-He400-N500-B</td>
<td>1108</td>
<td>0.45</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\(^a\)BET method with Rouquerol criterion. \(^b\)DR method. \(^c\)Difference between the total pore volume calculated at \( p/p_0 = 0.99 \) and the DR micropore volume.

The samples treated with NH\(_3\) at 400 and 500 °C (AC-He400-N400, AC-He400-N500 and AC-N500) show negligible loss of SSA (1.15 to 1.91% of loss) and pore
volume (1.37 to 1.49% of loss) compared to their predecessor samples, while the one treated at 600 °C (AC-He400-N600) has a greater loss with respect to his predecessor (3.69 and 2.99% loss of SSA and total pore volume respectively). Anyway, the reported losses are within the error of the BET methodology (10%).

The samples doped with boron reduced their SSA in the range of 16.15-33.40% and their pore volume in the range of 19.18-34.32% compared to their predecessors. These reductions can be attributed to the obstruction of the pores with boron species since the decrease is higher than what could be expected merely by the presence of boron oxide (5%). It can be noticed that the treatment with helium at 400 °C applied to the samples after boron doping did not help to clear the pores. The SSA and pore volume of the AC-He400-B sample remained almost constant after the treatment with helium (AC-He400-B-He400 sample), while the AC-B sample lost 21.82% of SSA and 22.03% of pore volume after the treatment (AC-B-He400). This loss of SSA can be caused by the diffusion of boron molecules into the pores. Finally, the treatment with NH$_3$ applied to the AC-He400-B sample, which produced the AC-He400-B-N500 sample, reduced the SSA by 18.53% and the pore volume by 20.45%.

The pore size distribution in the micropore range was determined with the Horvath-Kawazoe model using nitrogen adsorption data. In Figure 3-2 the micropore distribution of the original sample (AC) is presented. The report indicates a median micropore width of 0.84 nm and a mean of 0.75 nm. This result shows that half of the micropores are in the size range of 0.65 to 0.84 nm, which is the optimal range for hydrogen adsorption (Geng et al., 2015; Im et al., 2008). Then, high hydrogen adsorption performance is expected for the AC sample and its derivatives.
3.2 Temperature-Programmed Decomposition

The release of CO, CO₂, and H₂O from the TPD analyses are presented in Figure 3-3. The CO release intensity curves of all samples are quite similar. Since the functional groups that release CO when decomposed have decomposition temperatures higher than 600 °C, the treatments at 200 and 400 °C are not expected to modify these functional groups (Figueiredo et al., 1999; Shafeeyan et al., 2010). The CO₂ release intensity curve of the AC sample has two peaks around 115 and 400 °C; the AC-He200 sample has a reduction of its first peak, and its second peak is similar to the second peak of the AC sample; and the AC-He400 sample has a reduction of both peaks. Above 600 °C the three CO₂ peaks are roughly the same.
These results are logical, because AC-He200 and AC-He400 samples are expected to have a reduction in their CO$_2$ release in the temperature ranges of RT-200 °C and RT-400 °C, respectively, due to the previous heat treatment. About the H$_2$O release intensity curves, it can be seen that the peaks at around 90 °C of the heat-treated samples were reduced as the temperature of treatment increased.

![Graphs of TPD curves for CO, CO$_2$, and H$_2$O](image)

Figure 3-3: TPD curves of the original and heat-treated samples a) CO, b) CO$_2$ and c) H$_2$O release

The main functional groups that the AC sample has are the carboxylic groups, which are related to the release of CO$_2$ and H$_2$O between 50 and 200 °C; lactone groups,
which are associated with CO$_2$ release between 250 and 600 °C; carbonyl and quinone groups, which are ascribed to the release of CO between 700 and 1000 °C. In addition, CO release at around 700 °C corresponds to a small concentration of ether groups (Figueiredo et al., 1999; Shafeeyan et al., 2010). The AC-He200 and AC-He400 samples have the same functional groups as the AC sample, but the AC-He200 has a lower concentration of carboxylic groups, and the AC-He400 has a lower concentration of carboxylic and lactone groups. The three samples present a similar concentration of carbonyl and quinone groups.

### 3.3 X-ray Photoelectron Spectroscopy

In Table III-2 the surface compositions of the AC, AC-He400, AC-N500, AC-He400-N500, AC-B, AC-B-He400, and AC-He400-B-He400 samples determined by XPS are presented. The elements reported are C, O, N, and B, and their concentrations are expressed as atomic percent (at.%). From Table III-2 it can be seen that the C at.% remains between 90.80 and 92.40% for the original sample and the samples treated with helium and/or ammonia, while the samples treated with boron show an important reduction in the C at.% This is caused by the incorporation of B and O atoms, which came from borax decahydrate molecules. Due to the helium treatment, the AC sample reduced its content of oxygen, while the nitrogen content remained almost constant. This reduction is attributed to the partial elimination of oxygenated functional groups.

As expected, the ammonia treatment increased the nitrogen at.% of the AC-N500 and AC-He400-N500 samples. The AC-N500 sample has a slightly higher content of nitrogen compared to the AC-He400-N500 sample, probably due to the higher
concentration of oxygenated functional groups, which react with NH$_3$, facilitating the incorporation of nitrogen-containing functional groups on the surface of the activated carbon (Laheäär et al., 2014).

The samples doped with boron have a B at.% between 4.20 and 6.00, and an O at.% of 12.80 to 16.20. As borax decahydrate contains B and O, increases in boron and oxygen concentrations were expected. The higher boron content of the AC-B-He400 sample may be due to the presence of boron clusters, which cover the carbon surface and alters the proportions of the elements analyzed (Lagos et al., 2009). This implies a lower concentration of C and a higher concentration of O and B detected by the XPS. One possible reason for this sintering process is that the boron particles have weak interactions with the surface of the carbon and with the oxygenated functional groups. Then, as there were no anchoring sites for boron, the heat treatment with helium caused the boron particles to sinter. In the case of the AC-He400-B-He400 sample, the first helium treatment reduced the content of oxygenated functional groups on its surface, generating anchoring sites for boron, which prevented the sintering during the second helium treatment. Also, the boron-doped samples do not show nitrogen content, possibly because boron covers the nitrogen functionalities.
The deconvolution of the N 1s spectrum is presented in Figure 3-4a. A maximum of two peaks were identified, and their positions with their respective assigned chemical species are shown in Table III-3. It can be seen that the main nitrogen functionalities identified on the surface of the samples are pyridone and pyrrole. Since the binding energies of pyridone and pyrrole groups are similar, both groups are identified together as pyridone/pyrrole. AC and AC-He400 samples have a 100% of pyridone/pyrrole species, while in AC-N500 and AC-He400-N500 samples pyridine groups were incorporated. This indicates that the ammonia treatment introduced nitrogen into the carbons in the form of pyridine, pyridone, and pyrrole. Quaternary and oxidized nitrogen species were not detected from XPS analysis.
Table III-3: N 1s data from XPS

<table>
<thead>
<tr>
<th>Species</th>
<th>Pyridine (≈ 398.5 eV)</th>
<th>Pyridone/Pyrrole (≈ 400.5 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>AC-He400</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>AC-N500</td>
<td>39.80</td>
<td>60.20</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>16.80</td>
<td>83.20</td>
</tr>
<tr>
<td>AC-B</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-B-He400</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-He400-B-He400</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The B 1s deconvolution is presented in Figure 3-4b. Two peaks were identified, and their positions with their respective assigned chemical species are shown in Table III-4, which indicates that boron is present as BCO$_2$ and B–O species. The main chemical species is BCO$_2$, and it is in the range of 53.80 to 80.70%. The AC-B sample has the lowest relative percentage of BCO$_2$ (53.80%), while the AC-B-He400 and AC-He400-B-He400 samples have over 70% of BCO$_2$. To understand the differences between the samples, it is important to remember the sample preparation procedure. In the first place, the AC and AC-He400 samples were impregnated with BDH and then dried at 80 °C. Because of this heat treatment, a fraction of the boron precursor was incorporated into the carbonaceous structure of the carbon (i.e., BCO$_2$ species), while the other fraction remained unbound to the carbon (i.e., B–O species). In the second place, the AC-B and AC-He400-B samples were treated with helium at 400 °C. This treatment caused the incorporation of a major part of the B–O species into the carbon matrix, which explains the higher concentration of BCO$_2$ species presented in AC-B-He400 and AC-He400-B-He400 samples (Balaji et al., 2019). Since XPS analyzes the outer surface and not the inner surface (pores), the difference in BCO$_2$ species concentrations between the AC-B-He400 and AC-He400-B-He400 samples may be due to differences in the sites of
boron incorporation. Probably, the AC-He400-B-He400 sample has more BCO$_2$ species incorporated within the pores than the AC-B-He400 sample.

Table III-4: B 1s data from XPS

<table>
<thead>
<tr>
<th>Species</th>
<th>BCO$_2$</th>
<th>B–O</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-He400</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-N500</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-B</td>
<td>53.80</td>
<td>46.20</td>
</tr>
<tr>
<td>AC-B-He400</td>
<td>80.70</td>
<td>19.30</td>
</tr>
<tr>
<td>AC-He400-B-He400</td>
<td>71.60</td>
<td>28.40</td>
</tr>
</tbody>
</table>

The deconvolution of the O 1s peak is presented in Figure 3-4c. More than two peaks were identified, and their positions with their respective assigned chemical species are shown in Table III-5. The surface of the AC sample shows anhydride/lactone (O–C=O), quinone/carbonyl (C=O) and ether/phenolic (C–O–) groups in similar concentrations. Compared to the AC sample, the AC-He400 sample has incorporated carboxylic groups (COOH), and the quinone/carbonyl groups were removed. The main groups on its external surface are ether/phenolic groups, with an abundance of 42.90%. About the nitrogen-doped activated carbons, the AC-N500 sample has mainly quinone/carbonyl groups (53.40%) with anhydride/lactone and carboxylic groups, while the AC-He400-N500 sample has mostly ether/phenolic groups (60.10%) with a contribution of anhydride/lactone groups. In addition, the AC-He400-N500 sample has chemisorbed water or oxygen, probably due to contamination of the sample. Finally, the boron-doped samples have a similar oxygenated functional groups composition. Their main functional groups are quinone/carbonyl, in a range of 55.70 to 86.90%, accompanied by ether/phenolic groups (13.10 to 44.30%).
As can be seen, these results differ from those of TPD. Some reasons that could explain these differences are that the XPS analysis only examines the composition of the outer surface and not the entire structure of the material as TPD does, and the deconvolution of the O 1s peak could have a high margin of error. Additionally, the borax decahydrate impregnations introduced oxygen into the materials, which can be detected at binding energies close to those of the oxygenated functional groups, interfering with the O 1s interpretation.

Table III-5: O 1s data from XPS

<table>
<thead>
<tr>
<th>Samples</th>
<th>Species</th>
<th>O–C=O 531.3 eV</th>
<th>C=O 532.3 eV</th>
<th>C–O– 533.5 eV</th>
<th>COOH 534.3 eV</th>
<th>H₂O/O₂ 536.2 eV</th>
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<tbody>
<tr>
<td>AC</td>
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<td>29.20</td>
<td>34.50</td>
<td>36.10</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-He400</td>
<td></td>
<td>34.70</td>
<td>0.00</td>
<td>42.90</td>
<td>22.3</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-N500</td>
<td></td>
<td>23.30</td>
<td>53.40</td>
<td>0.00</td>
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<td>0.00</td>
<td>60.10</td>
<td>0.00</td>
<td>29.60</td>
</tr>
<tr>
<td>AC-B</td>
<td></td>
<td>0.00</td>
<td>74.90</td>
<td>25.10</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-B-He400</td>
<td></td>
<td>0.00</td>
<td>86.90</td>
<td>13.10</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC-He400-B-He400</td>
<td></td>
<td>0.00</td>
<td>55.70</td>
<td>44.30</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 3-4: XPS deconvolution curves of the a) N 1s, b) B 1s and c) O 1s peaks of the analyzed samples
3.4 Density-Functional Theory

Only the results of pyridine, pyridone, pyrrole, quaternary nitrogen and graphene sites are reported, because the XPS analysis did not detect other nitrogen functionalities and the quaternary nitrogen presented the highest adsorption energy. Pyridine groups correspond to the D, E and F sites (see Figures 2-12 and 2-13); pyridone groups correspond to the I site; pyrrole groups correspond to the L site; quaternary nitrogen groups correspond to the H site; and the graphene structure corresponds to the C site.

The analyzed complexes are presented in Table III-6, which shows low adsorption energy values. These results are reasonable since physisorption occurs through weak interactions (Van der Waals forces). The final states of the different complexes determined by the DFT adsorption model are presented in Figure 3-5.

Table III-6: Absolute value of the adsorption energies ($E_{ads}$) and shortest interatomic distances between H$_2$ and the ACL of the different complexes

| Adsorption complexes | $|E_{ads}|$ (kJ/mol) | Final H$_2$-ACL distance (Å) |
|----------------------|---------------------|-----------------------------|
| C1 (graphene)        | 4.52                | 3.21                        |
| C2 (graphene)        | 5.11                | 3.12                        |
| D1 (internal pyridine)| 5.32               | 2.93                        |
| E1 (internal pyridine)| 3.68               | 3.10                        |
| F1 (edge pyridine)   | 4.98                | 3.12                        |
| H1 (quaternary nitrogen) | 7.91           | 3.00                        |
| I1 (pyridone)        | 5.57                | 3.06                        |
| I2 (pyridone)        | 6.03                | 3.16                        |
| L1\(^{a}\) (pyrrole) | 5.11                | 3.19                        |

\(^{a}\) In the case of the L1 complex, an H atom was added to the pyrrolic group of the ACL (i.e., A site protonation).
Regarding geometry aspects, hydrogen molecules were adsorbed parallel to the activated carbon layer (ACL), which is more favorable than the perpendicularly adsorbed mode (Okamoto & Miyamoto, 2001). In the case of D1 complex, H$_2$ shows a steep angle with respect to the layer material when it is adsorbed, which differs from the rest of the complexes. As far as the distances are concerned, all complexes ended with an elongation of the initial distances between H$_2$ and ACL structure, with
distances around 3 Å. In addition, all adsorbed H₂ complexes had an H–H bond distance of 0.74 Å, which agrees with the experimental data reported for H₂ (Huber & Herzberg, 1979).

The adsorption of H₂ at some sites was more favorable than at others, even when the hydrogen molecules were placed in the same orientation. The adsorption complexes were sensitive to the initial position of hydrogen, being those with the initial position of H₂ on the bridge sites the most stable, *i.e.*, over and along the bond between atoms (as C2 and H1 complexes). Although some initial positions of the complexes started near O atoms, in all cases H₂ was displaced to positions over the proximal C or N atoms.

The hydrogen adsorptions of the C1 and C2 complexes are not as favorable as those of other complexes. This could be attributed to the position of H₂, over a hollow site versus a bridge site (over the C–C bond). However, a different case happens if the adsorption is over sites with/or near N atoms, which is in line with experimental data and with other theoretical studies (Fujimoto & Saito, 2014; Petrushenko & Petrushenko, 2019). It has been described that the application of electric fields could favor the hydrogen adsorption on graphene due to the reduction of its energy barrier, with an effect similar to that caused by the presence of nitrogen-containing groups (Jain & Kandasubramanian, 2019; Zhimin & Sean, 2011). This fact could explain the higher adsorption energy calculated at the H site of the material, which has charged nitrogen atoms (N⁺). The H1 complex, which models a quaternary nitrogen group, reached the greatest adsorption energy among the complexes, and it has more than 1.5 times the adsorption energy of the graphene layer. For this reason, it would be interesting to develop a methodology to incorporate quaternary nitrogen groups into activated carbons, to increase the adsorption of hydrogen.
About the adsorption over pyridine groups, E1 and F1 complexes show to be less favorable compared with D1 complex. As the C1 complex, the initial position of H₂ in the E1 complex over the hollow site generates a weaker interaction than the one obtained with the D1 and F1 complexes. In addition, the DFT results suggest that the inner pyridine groups (i.e., D1 complex) are better than the edge pyridine groups (i.e., F1 complex) for hydrogen adsorption, as the calculated adsorption energy of the D1 complex is greater.

Regarding pyridone groups, the I2 complex has higher adsorption energy than the I1 complex, probably because in the I2 complex the H₂ molecule is more aligned to the bond between carbon atoms. In addition, H₂ moves away from the oxygen atom, getting closer to the carbon atom that is next to the nitrogen atom. In the case of the pyrrole group, the adsorption energy of the L1 complex is like the energies of the C2 and D1 complexes, and it is weaker than the energies of the pyridone groups (I1 and I2 complexes).

Among the nitrogen functionalities detected by the XPS analysis, the DFT study concludes that pyridone groups have the greatest hydrogen adsorption energies. For this reason, any increment in pyridone groups concentration will help increase the adsorption of hydrogen on activated carbons.

### 3.5 Hydrogen Storage

#### 3.5.1 Experimental results

The hydrogen adsorption isotherms performed at 77 K and up to 0.93 bar are presented in Figure 3-6, and the maximum adsorptions are summarized in Table III-7. The adsorption of the AC sample was performed three times to estimate the relative error of the measurements, which was less than 2%.
Figure 3-6: Hydrogen excess adsorption isotherms at 77 K and up to 0.93 bar of the a) original (AC) and heat-treated samples, b) ammonia-treated samples, c) boron-treated samples, and d) ammonia/boron-treated samples
Table III-7: Hydrogen excess adsorption and hydrogen excess adsorption normalized per SSA of the different activated carbon samples at 77 K and 0.93 bar

<table>
<thead>
<tr>
<th>Samples</th>
<th>$H_2$ adsorption (wt%)</th>
<th>$H_2$ adsorption/SSA (wt%/($m^2g^{-1}$) ∙ 1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1.98</td>
<td>1.18</td>
</tr>
<tr>
<td>AC-He200</td>
<td>1.81</td>
<td>1.19</td>
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<tr>
<td>AC-He400</td>
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<td>1.15</td>
</tr>
<tr>
<td>AC-N500</td>
<td>2.14</td>
<td>1.30</td>
</tr>
<tr>
<td>AC-He400-N400</td>
<td>2.10</td>
<td>1.35</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>2.34</td>
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</tr>
<tr>
<td>AC-He400-N600</td>
<td>1.90</td>
<td>1.26</td>
</tr>
<tr>
<td>AC-B</td>
<td>1.68</td>
<td>1.19</td>
</tr>
<tr>
<td>AC-B-He400</td>
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<td>1.71</td>
</tr>
<tr>
<td>AC-He400-B</td>
<td>1.40</td>
<td>1.34</td>
</tr>
<tr>
<td>AC-He400-B-He400</td>
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<td>1.73</td>
</tr>
<tr>
<td>AC-He400-B-N500</td>
<td>1.33</td>
<td>1.56</td>
</tr>
<tr>
<td>AC-He400-N500-B</td>
<td>1.69</td>
<td>1.53</td>
</tr>
</tbody>
</table>

The hydrogen adsorption in the undoped samples decreased as the heat treatment was applied, going from 1.98 wt% for the AC sample to 1.81 wt% for the AC-He200 and AC-He400 samples. These reductions are attributed to the loss of textural properties (SSA and pore volume), which is produced by the reduction of surface functionalities and the collapse of the physical structure. The hydrogen adsorbed per area (i.e., wt%/SSA) was almost the same between the samples, suggesting that the presence of carboxylic and lactone oxygenated functional groups does not play an important role in hydrogen adsorption at 77 K.
For the N-doped samples, the results were not like the tendency shown before, and the changes in hydrogen adsorption were not directly related to the textural properties of the materials. The AC-N500 sample displayed the highest SSA and pore volume, but it had hydrogen adsorption of 2.14 wt%, while the AC-He400-N500 sample had hydrogen adsorption of 2.34 wt%. This result suggests that the previous thermal treatment of activated carbon at 400 °C and subsequent nitration with NH₃ at 500 °C favors the hydrogen adsorption.

If the results of XPS analysis are considered, the differences between both samples are the N at.% and the concentration of pyridine, pyridone and pyrrole species. The AC-N500 sample has 1.60 at.% of nitrogen on its surface, while the AC-He400-N500 sample has 1.10 at.%. Since the nitrogen concentration seems to be favorable for the hydrogen adsorption, and as the AC-N500 sample has more nitrogen on its surface, it should achieve higher adsorption, but this did not happen. Then, a difference in the concentration of nitrogen species should explain these hydrogen adsorption results. The AC-He400-N500 sample has a lower concentration of pyridine species than the AC-N500 sample (16.80 versus 39.80% respectively), and it has a greater concentration of pyridone/pyrrole species (83.20 versus 60.20 respectively). In addition, the DFT results suggested that pyridone has a higher hydrogen adsorption energy than pyridine and pyrrole groups. Therefore, it can be assumed that the AC-He400-N500 sample has a greater contribution of pyridone species, which explains its higher hydrogen adsorption.

The AC-He400-N400 and AC-He400-N600 samples had adsorptions of 2.10 and 1.90 wt%, respectively, which indicates that the temperature of NH₃ treatment influenced the hydrogen adsorption. If the hydrogen adsorptions and the NH₃ doping temperatures of the AC-He400-N400, AC-He400-N500, and AC-He400-N600 samples are related by a quadratic equation, as shown in Figure 3-7, maximum adsorption of 2.34 wt% can be found at 486 °C. This maximum point is quite close
to the hydrogen adsorption and the doping temperature of the AC-He400-N500 sample, this could suggest that the sample is almost at the optimal point of the NH₃ doping procedure applied in this study.

Figure 3-7: Quadratic relation between the adsorption of hydrogen and the NH₃ doping temperature of the AC-He400-N400, AC-He400-N500 and AC-He400-N600 samples

Table III-7 shows that all samples treated with NH₃ increased their normalized hydrogen adsorption capacity per area, suggesting that NH₃ favors H₂ adsorption in agreement with Giraudet et al. (2011). These results are contradictory to those reported by other authors (Kang et al., 2009; Zhao et al., 2013).

As far as respect to the boron doping is concerned, all the B-doped samples had lower hydrogen adsorption capacities than the AC sample. The AC-B sample had a reduction of 15.15% in contrast with its predecessor (AC sample), and the AC-He400-B sample reduced its hydrogen adsorption capacity by 22.65% compared to
its precursor (AC-He400 sample). These reductions in hydrogen storage were attributed to the loss of SSA and pore volume since the hydrogen adsorbed per area \((i.e., \text{wt}\%/\text{SSA})\) increased. Despite these reductions, something interesting happened with the post-treatment with helium. AC-B-He400 and AC-He400-B-He400 samples presented an increment of 11.90 and 24.29\% in hydrogen adsorption compared to their predecessors (AC-B and AC-He400-B samples). However, the AC-B-He400 sample had 21.82\% less SSA than the AC-B sample, and the AC-He400-B and AC-He400-B-He400 samples have practically the same SSA.

The effect in hydrogen adsorption caused by the helium treatment applied to the B-doped samples can be understood based on the XPS analysis results. It was concluded that the helium treatment applied to the B-doped samples increased the incorporation of boron molecules into the carbon matrix \((i.e., \text{BCO}_2\) species), reducing the concentration of B–O species. Because of this incorporation, a stronger interaction between boron and the carbonaceous structure was produced, which increased the electron density distortions on the surface of the material caused by boron. Indeed, when boron is introduced into a carbon framework, the surface of the material becomes polarized and electron-deficient sites are generated, increasing the interactions between the hydrogen molecules and the surface (Kopac \textit{et al.}, 2020; Kuchta \textit{et al.}, 2010; Shcherban \textit{et al.}, 2017; Zhu \textit{et al.}, 2005).

If the results of the B-doped samples are analyzed in terms of hydrogen adsorbed per area \((i.e., \text{wt}\%/\text{SSA})\), the AC-B-He400, AC-He400-B and AC-He400-B-He400 samples presented increases of 44.92, 13.56 and 46.61\%, respectively, if compared with the AC sample. This suggests that if boron is applied to an activated carbon without losing textural properties (SSA and pore volume), an increase in hydrogen adsorption as high as 46\% could be reached.
The results obtained with the activated carbons doped with borax decahydrate contradict the results presented by Kopac et al. (2020). The authors reported that the SSA was maintained or increased by the borax decahydrate doping with an increment in hydrogen adsorption from 2.35 to 4.14 wt%, while in this study, the SSA decreased with a reduction in hydrogen adsorption.

Regarding nitrogen and boron doping, the AC-He400-B-N500 sample reduced its hydrogen adsorption by 5.00% in comparison with the AC-He400-B sample. However, the hydrogen adsorption per area (i.e., wt%/SSA) had an increment of 16.42%, which means that nitrogen doping influenced the adsorption. The AC-He400-N500 sample reduced its hydrogen adsorption capacity in a 27.78% after the boron doping, resulting in the AC-He400-N500-B sample. Despite this reduction, the hydrogen adsorption per area remained almost the same, suggesting that the boron doping did not have much influence on the hydrogen adsorption. This behavior could be attributed to the loss of SSA, and no synergistic effects between nitrogen and boron were appreciated.

### 3.5.2 Modified Dubinin-Astakhov model application

The modified Dubinin-Astakhov (MDA) adsorption model was fitted to the adsorption isotherm of the AC-He400-N500 sample. The fit of the model to the experimental data was quite accurate, with a coefficient of determination ($R^2$) of almost 1.00. Figure 3-8 shows the hydrogen adsorption isotherms of the experimental data and the fitted MDA model, and as can be seen, both isotherms are practically equal, one covering the other. The parameters and the coefficient of determination of the fit are listed in Table III-8. It is important to notice that the adsorption volume ($V_a$) value is pretty close to the micropore volume obtained from
the nitrogen adsorption isotherm (0.65 cm$^3$/g). Then, it can be concluded that adsorption takes place almost completely in the micropore volume.

Figure 3-8: Hydrogen excess adsorption isotherms of the experimental data and MDA model fit for the AC-He400-N500 sample

Table III-8: Parameters and coefficient of determination of the MDA model fit

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{max}$ (wt%)</td>
<td>14.46</td>
</tr>
<tr>
<td>$P_0$ (bar)</td>
<td>1889.26</td>
</tr>
<tr>
<td>$\alpha$ (J/mol)</td>
<td>2248.04</td>
</tr>
<tr>
<td>$\beta$ (J/(mol·K))</td>
<td>14.41</td>
</tr>
<tr>
<td>$m$</td>
<td>1.60</td>
</tr>
<tr>
<td>$V_a$ (cm$^3$/g)</td>
<td>0.64</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999965</td>
</tr>
</tbody>
</table>
Applying the MDA model with the parameters presented above, the hydrogen adsorption isotherm was extrapolated up to 100 bar pressure. This extrapolation is presented in Figure 3-9. The excess adsorption has its greatest increment in the low-pressure range, going from 2.39 wt% at 1 bar to 6.10 wt% at 20 bar, and as the pressure gets close to 100 bar the isotherms begin to approach an upper limit, reaching 7.73 wt% at 100 bar.

![Graph showing hydrogen excess adsorption isotherm](image)

**Figure 3-9**: Hydrogen excess adsorption isotherm of the MDA model extrapolated up to 100 bar pressure (77 K) for the AC-He400-N500 sample

Using this extrapolation and knowing the densities of the AC-He400-N500 sample (Table III-9), Equation 2.18 can be used to determine the hydrogen storage density of a tank filled with the sample. Figure 3-10 presents three isotherms expressed on a volumetric basis (kg/m³), the grey one corresponds to the hydrogen stored by compression inside the tank with the adsorbent, the orange one is the excess adsorption, and the blue one is the total amount stored, which is the sum of the first two isotherms. The total hydrogen storage, the excess hydrogen adsorption, and the compressed hydrogen reach values of 61.09, 40.80, and 20.29 kg/m³, respectively,
at 77 K and 100 bar. At this point, the contribution of the excess adsorption is about 67% of the total hydrogen storage, while compressed hydrogen contributes about 33%. At low pressures (0-10 bar), the total hydrogen storage is mainly due to adsorption, and as the pressure rises, the contribution of the excess adsorption begins to stagnate, while the contribution of the compression keeps increasing. This is caused by the saturation of the adsorption sites.

Table III-9: Bulk and skeletal densities of the AC-He400-N500 sample

| Density (kg/m³) |  
|----------------|-----------------|
| $\rho_a$       | 528             |
| $\rho_{He}$    | 1500            |

Figure 3-10: Hydrogen storage densities at 77 K and up to 100 bar in a tank filled with AC-He400-N500 (using the MDA extrapolation): total hydrogen storage, excess hydrogen adsorption and compressed hydrogen.
Figure 3-11 shows the comparison of hydrogen storage in a tank filled with the adsorbent and another without the adsorbent. The tank filled with the AC-He400-N500 sample reaches hydrogen storage of 61.09 kg/m$^3$, while an empty tank achieves 31.30 kg/m$^3$ at 77 K and 100 bar pressure. Then, a tank filled with AC-He400-N500 would store 1.95 times more hydrogen than an empty tank operating under those conditions. For reference, when hydrogen is stored by compression at 700 bar and RT, its density is about 39 kg/m$^3$, and the density of liquid hydrogen is 71 kg/m$^3$. Then, the proposed hydrogen adsorption system would have a higher hydrogen density than compressed hydrogen, and it would be close to liquid hydrogen.

![Graph showing hydrogen storage density](image)

Figure 3-11: Hydrogen storage density at 77 K and up to 100 bar of a tank filled with AC-He400-N500 (using the MDA extrapolation) versus an empty tank

Although the estimated hydrogen densities were comparable with compressed and liquid hydrogen, the weight of the storage system is a relevant parameter that must be considered. The gravimetric storage density of the AC-He400-N500 sample, considering the adsorbed and compressed hydrogen, is presented in Figure 3-12. At
100 bar pressure, the gravimetric storage density reaches a value of 11.57 wt%. In addition, the weight of the tank must be considered to assess the gravimetric hydrogen storage density of the entire system. Then, the gravimetric storage density of the system will be lower than 11.57 wt%. For example, if a storage tank of 150 liters weighing 100 kg is filled with the AC-He400-N500 sample to store hydrogen at 77 K and 100 bar, the gravimetric storage density of the system will be about 5.11 wt%.

![Gravimetric hydrogen storage density at 77 K and up to 100 bar of the AC-He400-N500 sample considering the adsorbed and compressed hydrogen (using the MDA extrapolation)](image)

Figure 3-12: Gravimetric hydrogen storage density at 77 K and up to 100 bar of the AC-He400-N500 sample considering the adsorbed and compressed hydrogen (using the MDA extrapolation)

### 3.5.3 Comparison with other studies

Table III-10 shows the results of hydrogen adsorption at 77 K on activated carbons and other carbonaceous materials reported by different authors. As can be seen, the undoped carbons tend to have lower specific adsorptions (i.e., wt%/SSA) in contrast
to the doped ones. Comparing the N-doped carbons of Giraudet et al. (2011) and Kang et al. (2009) with the AC-He400-N500 sample, their samples had higher hydrogen adsorption capacities, but these adsorptions were carried out at pressures up to 30 and 15 bar, respectively. Then, if the adsorption of the AC-He400-N500 sample is assessed at higher pressures, it will probably perform better than those samples. Indeed, the MDA model indicates that the AC-He400-N500 sample adsorbs 5.69 and 6.65 wt% of hydrogen at 15 and 30 bar, respectively. Regarding the B-doped carbons, the samples developed in this study had a better performance in hydrogen adsorption in comparison with the sample of Shcherban et al. (2017).
Table III-10: Comparison of hydrogen excess adsorption capacities and hydrogen excess adsorption normalized per SSA at 77 K reported in different studies. Hydrogen adsorption values at 1, 15, and 30 bar were estimated based on the MDA model and are marked with an asterisk. The estimated values at 1 bar are presented in parentheses.

<table>
<thead>
<tr>
<th>Samples</th>
<th>H$_2$ adsorption (wt%)</th>
<th>H$_2$ adsorption/SSA (wt%/ (m$^2$ g$^{-1}$) · 1000)</th>
<th>Pressure (bar)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>2.74</td>
<td>0.87</td>
<td>1.00</td>
<td>Zhao et al., 2019</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>3.21</td>
<td>0.86</td>
<td>1.00</td>
<td>Geng et al., 2015</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>2.36</td>
<td>0.85</td>
<td>1.00</td>
<td>Geng et al., 2015</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1.92</td>
<td>1.09</td>
<td>1.00</td>
<td>Geng et al., 2015</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>4.11</td>
<td>1.84</td>
<td>1.00</td>
<td>1.00 Kopac et al., 2020</td>
</tr>
<tr>
<td>Zeolite templated carbon</td>
<td>2.04</td>
<td>0.54</td>
<td>1.00</td>
<td>Geng et al., 2015</td>
</tr>
<tr>
<td>N-doped carbon</td>
<td>2.91</td>
<td>0.89</td>
<td>1.00</td>
<td>Zhao et al., 2019</td>
</tr>
<tr>
<td>N-doped carbon</td>
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<td>2.97</td>
<td>30.00</td>
<td>Giraudet et al., 2011</td>
</tr>
<tr>
<td>N-doped carbon xerogel</td>
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<td>2.02</td>
<td>15.00</td>
<td>Kang et al., 2009</td>
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<tr>
<td>B-doped carbon</td>
<td>1.20</td>
<td>1.37</td>
<td>1.00</td>
<td>1.00 Shcherban et al., 2017</td>
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<td>N&amp;B-doped carbon</td>
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<td>Kopac et al., 2020</td>
</tr>
<tr>
<td>AC</td>
<td>1.98 (2.02*)</td>
<td>1.18 (1.21*)</td>
<td>0.93 (1.00)</td>
<td>This study</td>
</tr>
<tr>
<td>AC-He400</td>
<td>1.81 (1.85*)</td>
<td>1.15 (1.18*)</td>
<td>0.93 (1.00)</td>
<td>This study</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>2.34 (2.39*)</td>
<td>1.50 (1.54*)</td>
<td>0.93 (1.00)</td>
<td>This study</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>5.69*</td>
<td>3.66*</td>
<td>15.00</td>
<td>This study</td>
</tr>
<tr>
<td>AC-He400-N500</td>
<td>6.65*</td>
<td>4.28*</td>
<td>30.00</td>
<td>This study</td>
</tr>
<tr>
<td>AC-B-He400</td>
<td>1.88 (1.92*)</td>
<td>1.71 (1.76*)</td>
<td>0.93 (1.00)</td>
<td>This study</td>
</tr>
<tr>
<td>AC-He400-B-He400</td>
<td>1.74 (1.78*)</td>
<td>1.73 (1.78*)</td>
<td>0.93 (1.00)</td>
<td>This study</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

In this study, different modification procedures based on helium, ammonia, and borax decahydrate treatments were developed and tested to improve the hydrogen adsorption of a commercial activated carbon. The 13 produced samples were analyzed by nitrogen adsorption/desorption isotherms, temperature-programmed decompositions, X-ray photoelectron spectroscopies, and hydrogen adsorption isotherms. In addition, the Modified Dubinin-Astakhov adsorption model, which was proposed by Richard et al. (2009), was applied to extrapolate the hydrogen adsorption experimental data of the AC-He400-N500 sample up to 100 bar pressure. Then, the extrapolation was used to calculate the total hydrogen storage density that could be achieved with a reservoir filled with the AC-He400-N500 sample, which would store hydrogen by adsorption and compression at 77 K and pressures up to 100 bar. A density-functional theory model was also developed to analyze the effect of the nitrogen functionalities on hydrogen adsorption and determine which functional groups favor adsorption to a greater extent. Based on the results, the established hypothesis was confirmed and five main conclusions can be drawn:

i) The reduction of the concentration of oxygenated functional groups on the surface of the AC sample did not help to improve the adsorption of hydrogen. The adsorption was reduced due to the loss of textural properties, and the adsorption per area (i.e., wt%/SSA) was maintained almost constant. It can thus be concluded that the concentration of carboxylic and lactone oxygenated functional groups does not play an important role in hydrogen adsorption at 77 K.

ii) The ammonia treatment proved to be favorable for the adsorption of hydrogen. Specifically, the AC-He400-N500 sample had the highest increase in adsorption,
increasing the adsorption by 18.18% in comparison to the AC sample (2.34 wt% versus 1.98 wt%). The AC-N500 sample reached a lower hydrogen adsorption (2.14 wt%) due to differences in the nitrogen functionalities. These improvements were obtained despite the loss of SSA, which means that the incorporation of nitrogen into activated carbons has a positive effect that counteracts the loss of specific surface area.

iii) Among the nitrogen functionalities detected by the XPS analysis, the DFT study concluded that pyridone groups have the greatest hydrogen adsorption energies (5.57 to 6.03 kJ/mol). This could explain the higher adsorption reached by the AC-He400-N500 sample. In addition, it was determined that quaternary nitrogen sites have adsorption energy of 7.91 kJ/mol. Then, it would be interesting to develop a modification procedure that introduces quaternary nitrogen into activated carbons, aiming to increase the adsorption of hydrogen.

iv) Hydrogen adsorption on the samples impregnated with borax decahydrate was reduced due to the loss of SSA. Anyway, the B-doped samples increased their adsorption per area by up to 46.61%. This means that if boron is applied to an activated carbon without losing textural properties, an increment in hydrogen adsorption as high as 46% can be reached. In addition, it was determined that the boron doping followed by a helium treatment improves the adsorption capacity of the B-doped samples, because it increases the incorporation of boron molecules into the carbon matrix, enhancing the interaction between boron and the carbonaceous structure.

v) The samples co-doped with nitrogen and boron had low hydrogen adsorption compared to the other samples doped only with nitrogen or boron. Synergistic effects between nitrogen and boron were not appreciated.
5. PROSPECTS FOR FUTURE WORK

There are many tasks to be carried out to continue with the development of this research.

The steps to follow are listed below:

i) Increase the treatment time with ammonia at 500 °C to evaluate if it improves hydrogen adsorption.

ii) Apply boron to the activated carbon samples through chemical vapor deposition with decaborane and assess the loss of SSA and the hydrogen adsorption.

iii) Study the adsorption capacities of the samples under high pressures (over 100 bar) and at different temperatures. This would allow verifying if the extrapolation carried out with the Modified Dubinin-Astakhov adsorption model was accurate, and it would allow studying the adsorption of hydrogen at room temperature and high pressures.

iv) Select the best sample for hydrogen adsorption and analyze its behavior over various adsorption/desorption cycles. This would allow determining the useful capacity of the system, since there is always a remnant of hydrogen when the system is discharged.

v) Perform an energetic analysis to calculate the adsorption energy of the samples. This can be done by applying the Clausius-Clapeyron equation.

vi) Finally, scale up the adsorption system using the best adsorbent and design a high-pressure tank to contain it.


APPENDIX
Appendix A: Nitrogen Adsorption/desorption isotherms of the carbonaceous materials

Appendix A1: Textural characteristics of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>SSA$^a$ (m²/g)</th>
<th>$V_0^b$ (cm³/g)</th>
<th>$V_m^c$ (cm³/g)</th>
<th>Carbon type and precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muestra de Pellets</td>
<td>1185</td>
<td>0.51</td>
<td>0.06</td>
<td>Pellet</td>
</tr>
<tr>
<td>Muestra de GC-1000</td>
<td>923</td>
<td>0.36</td>
<td>0.02</td>
<td>Granular</td>
</tr>
<tr>
<td>Muestra de GC-1000-He200</td>
<td>888</td>
<td>0.35</td>
<td>0.01</td>
<td>Granular</td>
</tr>
<tr>
<td>Muestra de GC-1000-He400</td>
<td>886</td>
<td>0.35</td>
<td>0.02</td>
<td>Granular</td>
</tr>
<tr>
<td>Aquactiv 12x40</td>
<td>1002</td>
<td>0.41</td>
<td>0.05</td>
<td>Granular</td>
</tr>
<tr>
<td>CG 1000 6x12</td>
<td>1152</td>
<td>0.47</td>
<td>0.03</td>
<td>Granular</td>
</tr>
<tr>
<td>China 1</td>
<td>8</td>
<td>0.00</td>
<td>0.03</td>
<td>Pellet - coal</td>
</tr>
<tr>
<td>China 2</td>
<td>37</td>
<td>0.02</td>
<td>0.04</td>
<td>Pellet - coal</td>
</tr>
<tr>
<td>China 3</td>
<td>1065</td>
<td>0.44</td>
<td>0.02</td>
<td>Granular - coconut</td>
</tr>
<tr>
<td>China 4</td>
<td>1120</td>
<td>0.46</td>
<td>0.02</td>
<td>Granular - coconut</td>
</tr>
<tr>
<td>Callaso</td>
<td>20</td>
<td>0.01</td>
<td>0.01</td>
<td>Biochar</td>
</tr>
<tr>
<td>Guano Vacuno</td>
<td>5</td>
<td>0.00</td>
<td>0.02</td>
<td>Biochar</td>
</tr>
<tr>
<td>Hierba del Platero</td>
<td>53</td>
<td>0.02</td>
<td>0.01</td>
<td>Biochar</td>
</tr>
<tr>
<td>Maiz</td>
<td>15</td>
<td>0.01</td>
<td>0.01</td>
<td>Biochar</td>
</tr>
<tr>
<td>Palma Dalitera</td>
<td>8</td>
<td>0.00</td>
<td>0.02</td>
<td>Biochar</td>
</tr>
<tr>
<td>Tomate</td>
<td>11</td>
<td>0.00</td>
<td>0.01</td>
<td>Biochar</td>
</tr>
</tbody>
</table>

$^a$ BET method with Rouquerol criterion. $^b$ DR method. $^c$ Difference between the total pore volume calculated at $p/p_0=0.99$ and the DR micropore volume.
Appendix A2: N$_2$ adsorption/desorption isotherms of the different samples

This appendix presents the nitrogen adsorption and desorption isotherms of the carbon materials that were not used as the main material in the study.
Appendix B: Temperature-programmed decomposition
Appendix C: Density-functional theory

Appendix C1: Absolute value of the adsorption energies ($E_{ads}$) and shortest interatomic distances between H$_2$ and the ACL of the different complexes

| Adsorption complexes          | $|E_{ads}|$ (kJ/mol) | Final H$_2$-ACL distance (Å) |
|------------------------------|---------------------|------------------------------|
| A1 (pyrrolic)                | 5.10                | 3.07                         |
| B1 (internal pyrrolic)       | 6.19                | 3.03                         |
| C1 (graphene)                | 4.52                | 3.21                         |
| C2 (graphene)                | 5.11                | 3.12                         |
| D1 (internal pyridine)       | 5.32                | 2.93                         |
| E1 (internal pyridine)       | 3.68                | 3.10                         |
| F1 (edge pyridine)           | 4.98                | 3.12                         |
| G1 (nitrogen oxides)         | 5.06                | 2.94                         |
| H1 (quaternary nitrogen)     | 7.91                | 3.00                         |
| I1 (pyridone)                | 5.57                | 3.06                         |
| I2 (pyridone)                | 6.03                | 3.16                         |
| J1 (nitrogen oxides)         | 5.44                | 2.96                         |
| J2 (nitrogen oxides)         | 5.44                | 3.11                         |
| K1 (amine)                   | 5.19                | 3.34                         |
| L1$^a$ (pyrrole)             | 5.11                | 3.19                         |

$^a$ In the case of the L1 complex, an H atom was added to the pyrrolic group of the ACL (i.e., A site protonation).
Appendix C2: Views of the final states of the different H$_2$-ACL complexes of the DFT model

<table>
<thead>
<tr>
<th>A1 (pyrrolic)</th>
<th>B1 (internal pyrrolic)</th>
<th>C1 (graphene)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="A1 (pyrrolic)" /></td>
<td><img src="image2.png" alt="B1 (internal pyrrolic)" /></td>
<td><img src="image3.png" alt="C1 (graphene)" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C2 (graphene)</th>
<th>D1 (internal pyridine)</th>
<th>E1 (internal pyridine)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4.png" alt="C2 (graphene)" /></td>
<td><img src="image5.png" alt="D1 (internal pyridine)" /></td>
<td><img src="image6.png" alt="E1 (internal pyridine)" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>F1 (edge pyridine)</th>
<th>G1 (nitrogen oxides)</th>
<th>H1 (quaternary nitrogen)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image7.png" alt="F1 (edge pyridine)" /></td>
<td><img src="image8.png" alt="G1 (nitrogen oxides)" /></td>
<td><img src="image9.png" alt="H1 (quaternary nitrogen)" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>I1 (pyridone)</th>
<th>I2 (pyridone)</th>
<th>J1 (nitrogen oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image10.png" alt="I1 (pyridone)" /></td>
<td><img src="image11.png" alt="I2 (pyridone)" /></td>
<td><img src="image12.png" alt="J1 (nitrogen oxides)" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J2 (nitrogen oxides)</th>
<th>K1 (amine)</th>
<th>L1 (pyrrole)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image13.png" alt="J2 (nitrogen oxides)" /></td>
<td><img src="image14.png" alt="K1 (amine)" /></td>
<td><img src="image15.png" alt="L1 (pyrrole)" /></td>
</tr>
</tbody>
</table>
Appendix D: Hydrogen storage

Appendix D1: Hydrogen adsorption isotherms at 77 K and up to 0.93 bar of the different samples

Appendix D2: Hydrogen adsorption of the different samples at 77 K and 0.93 bar

<table>
<thead>
<tr>
<th>Samples</th>
<th>H$_2$ adsorption (wt%)</th>
<th>H$_2$ adsorption/SSA (wt%/($m^2g^{-1}$) · 1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muestra de Pellets</td>
<td>1.14</td>
<td>0.97</td>
</tr>
<tr>
<td>Muestra de GC-1000</td>
<td>1.48</td>
<td>1.60</td>
</tr>
<tr>
<td>Muestra de GC-1000-He200</td>
<td>1.49</td>
<td>1.68</td>
</tr>
<tr>
<td>Muestra de GC-1000-He400</td>
<td>1.49</td>
<td>1.68</td>
</tr>
<tr>
<td>Aquactiv 12x40</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td>CG 1000 6x12</td>
<td>1.67</td>
<td>1.45</td>
</tr>
<tr>
<td>China 4</td>
<td>1.46</td>
<td>1.31</td>
</tr>
</tbody>
</table>
Appendix D3: Redlich-Peterson hydrogen adsorption isotherms at 77 K and up to 0.93 bar of the different samples

This appendix presents the Redlich-Peterson model fit of the hydrogen adsorption of the different samples.

![Graphs showing hydrogen adsorption isotherms for different samples](image-url)