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CO₂ CAPTURE FROM FLUE GASES BY ELECTRIC SWING ADSORPTION

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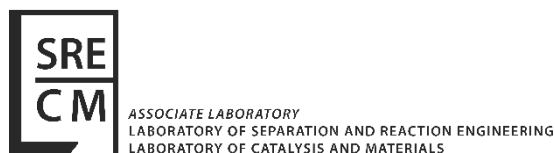
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“Gratidão é saber reconhecer”

Desafios, convicções, dificuldades, aprendizagem e superação; são estas as palavras que me ocorrem para definir o meu percurso ao longo destes 4 anos. Como tal e por acreditar vivamente que para conseguirmos produzir valor a nível profissional, necessitamos primeiro de criar valor em nós próprios, são várias as pessoas a quem quero deixar uma palavra de agradecimento pelo valor que criaram em mim e no meu trabalho.

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ABSTRACT

In this work, the development of hybrid materials suitable to be used in Electric Swing Adsorption (ESA) process was studied, in order to be applied in carbon dioxide capture from flue gases of post combustion processes used in industrial power plants.

First, methods for materials shaping were implemented, resulting in three different types of hybrid adsorbents produced.

A cooperation between FEUP and University of Tsinghua, in China, resulted in the production of a hybrid honeycomb monolith adsorbent with 70% of zeolite 13X and 30% of activated carbon by extrusion process. Adsorption equilibrium isotherms of CO₂ and N₂ were evaluated at different temperatures (303, 333 and 373 K) in a low-pressure range (0 to 1.5 bar). Adsorption kinetics were studied by single and binary breakthrough curve experiments. The CO₂/N₂ selectivity of this material was 54.0, considering multicomponent adsorption of a 20%/80% CO₂/N₂ mixture at 2.4 bar and 298 K. However, this material demonstrated to have high electrical resistivity and could not be heated by Joule effect under the conditions employed in the laboratory. Consequently, it was not suitable to be employed in ESA processes.

One of the methods implemented in the laboratory for adsorbents shaping was the extrusion process. In this context, four types of pellets were produced with different amounts of raw materials (activated carbon and zeolite 13X), carboxymethylcellulose as binder and water as solvent: pellets with 100% of activated carbon, pellets composed by 70% of activated carbon and 30% of zeolite 13X, pellets with 50% of activated carbon and 50% of zeolite 13X and pellets composed by 30% of activated carbon and 70% of zeolite 13X. An extensive study was done with these adsorbent materials, in terms of characterization, adsorption equilibrium of CO₂ and N₂ and adsorption kinetics. The CO₂/N₂ selectivity of the pellets was 62.8, 41.9, 24.6, 12.2 at 1.5 bar and 298 K, respectively for the 30%AC-70%13X, 50%AC-50%13X, 70%AC-30%13X and 100%AC pellets, considering a multicomponent adsorption of 20% of CO₂ in N₂. The results also showed that all the pellets demonstrated an increase of temperature when an electric current was applied, with the exception of pellets with 30% of activated carbon and 70% of zeolite 13X, concluding that these ones were not suitable for ESA process. For the other pellets produced, binary breakthrough curves with and without electrification in the

desorption step were performed. It was proved that the heating by joule effect resulted in a significant faster regeneration of the adsorbent.

In addition, an Electric Swing Adsorption cycle including four steps, which were, feed, using a stream of 25% of CO₂, electrification in a closed-column, to increase temperature, counter-current blowdown and counter-current purge with a recycle, was simulated using 100%AC pellets and 50%AC-50%13X pellets. Simulations performed using the 100%AC pellets allowed to obtain a 32.0% of purity and 29.2% of recovery for CO₂. When 50%AC-50%13X pellets were considered, this cycle allowed to obtain a CO₂ purity of 63.7% and a recovery of 43.3%.

3D-printing process, namely Direct Ink Writing method, was implemented and used to develop a hybrid 3D-printed honeycomb monolith composed by 70% of zeolite 13X and 30% of activated carbon. The adsorbent was successfully printed with dimensions of 30×30×43 mm. CO₂ and N₂ adsorption equilibrium isotherms measurements were performed, demonstrating the high CO₂ capacity of this material (1.45 mol·kg⁻¹ at 0.09 bar and 303 K) and high selectivity for CO₂/N₂ separations (122.1 at 1.5 bar and 298 K).

Breakthrough experiments were carried out and well predicted by the implemented mathematical model. However, a poor temperature increase during electrification step was verified in the 30×30×43 mm honeycomb monolith using the maximum allowed current (about 20 A) with the available power supply unit. Smaller 3D-printed honeycomb monoliths (10×10×4 mm) were heated during 180 s, using a constant voltage of 25 V, resulting in a temperature increase of about 80 K.

RESUMO

Neste trabalho, foi estudado o desenvolvimento de novos materiais híbridos para o processo de Electric Swing Adsorption, a fim de serem usados na captura de dióxido de carbono em correntes dos processos de pós-combustão das centrais elétricas industriais.

Em primeiro lugar, foram implementados métodos para a preparação de materiais adsorventes, resultando na produção e no teste de três materiais diferentes.

Fruto de uma cooperação entre a FEUP e a Universidade de Tsinghua na China, foi produzido por extrusão um adsorvente híbrido na forma de monólito com estrutura de favo de mel com 70% de zeólito 13X e 30% de carvão ativado. Foram avaliadas as isotérmicas de equilíbrio de adsorção do CO_2 e do N_2 a diferentes temperaturas (303, 333 e 373 K), numa gama de pressões baixa. O material apresentou uma seletividade CO_2/N_2 de 54.0 a 298 K e 2.4 bar, considerando uma adsorção multicomponente de uma mistura de 20%/80% CO_2/N_2 . A cinética de adsorção foi estudada a partir das curvas de quebra. Este material demonstrou ter uma elevada resistividade elétrica e, por isso, não foram realizados ciclos de ESA.

Um dos métodos implementados no laboratório para desenvolver materiais estruturados foi o processo de extrusão. Neste contexto, foram produzidos quatro tipos de extrudados com diferentes quantidades de matérias-primas (carvão ativado e zeólito 13X), carboximetilcelulose usado como aglutinador e água como solvente : extrudados com 100% de carvão ativado, extrudados compostos por 70% de carvão ativado e 30% de zeólito 13X, extrudados com 50% de carvão ativado e 50% de zeólito 13X e extrudados compostos por 30% de carvão ativado e 70% de zeólito 13X. Foi realizado um vasto estudo com estes materiais, em termos de caracterização, equilíbrio de adsorção de CO_2 e N_2 e cinética de adsorção. Os valores de seletividade CO_2/N_2 foram de 62.8, 41.9, 24.6, 12.2 a 298 K e 1.5 bar, para os extrudados 30%AC-70%13X, 50%AC-50%13X, 70%AC-30%13X e 100%AC, respetivamente. Os resultados demonstraram que todos os extrudados, quando submetidos a uma corrente elétrica, aumentaram a temperatura, exceto os extrudados compostos por 30% de carvão ativado e 70% de zeólito 13X, concluindo assim que estes não são aplicáveis para processos de ESA. Para os outros extrudados, foram realizadas curvas de quebra binárias com e sem eletrificação na etapa de dessorção. Foi

demonstrado que o aquecimento por efeito de Joule resulta numa regeneração significativamente mais rápida.

Adicionalmente, um ciclo de Electric Swing Adsorption foi simulado usando os extrudados com 100%AC e outro usando os extrudados com 50%AC-50%13X, incluindo quatro etapas, que foram, a alimentação, usando uma corrente de 25% de CO₂, eletrificação em coluna fechada, despressurização contracorrente e purga contracorrente com reciclo. As simulações realizadas com os extrudados 100%AC permitiram obter uma pureza de CO₂ de 32.0% e uma recuperação de 29.2%. Considerando extrudados de 50%AC-50%13X, foi possível obter uma pureza 63.7% de CO₂ com 43.3% de recuperação.

Outro método implementado para preparação de materiais estruturados foi a impressão 3D, nomeadamente o processo de Direct Ink Writing. Com este método, um monólito 3D híbrido com estrutura de favo de mel composto por 70% de zeólito 13X e 30% de carvão ativado de dimensões 30×30×43 mm foi desenvolvido com sucesso. As medições das isotérmicas de equilíbrio de adsorção de CO₂ e do N₂ demonstraram uma grande capacidade de adsorção de CO₂ neste material (1.45 mol·kg⁻¹ a 0.09 bar e 303 K) e uma alta seletividade para separações CO₂/N₂ (122.1 a 1.5 bar e 298 K). As curvas de rutura simples e binárias realizadas experimentalmente foram bem previstas pelo modelo matemático implementado e demonstraram o fraco aquecimento do material durante a etapa de eletrificação no monólito com 30×30×43 mm, comprometendo o efeito de Joule. Monólitos 3D com dimensão 10×10×4 mm foram aquecidos durante 180 s usando uma voltagem constante de 25 V, resultando num aumento de temperatura de 80 K, aproximadamente.

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1 RELEVANCE AND MOTIVATION

Carbon dioxide is present in the atmosphere and is part of a natural circulation among the atmosphere, oceans, soil, plants, and animals. In contrast to natural effects, human activities interfere with this biological cycle due to the extracting activities of fossil fuels from deep below the earth's surface which have high concentrations of carbon, burning them for energy. The mixture between this carbon and oxygen leads to a combustion process, that generates even more carbon dioxide than would have naturally been present.

Industrial Revolution period was a mark in fossil fuels utilization as energy sources. Since this period, the energy demand has not stopped growing. Power generation and carbon-intensive industries are responsible for a large share of the anthropogenic CO₂ emissions to the atmosphere. Actually, fossil fuels fired power plants account for more than 80% of the total energy production worldwide [1].

Carbon dioxide is the primary gas emitted from human activities and the best-known greenhouse gas contributing to global warming. This makes fossil fuel burning power plants one of the main targets for reducing CO₂ emissions.

These emissions have been leading to a steady temperature rise all around the world, and these climate changes are a global concern. An evidence of this concern is the Paris agreement, negotiated within the United Nations Framework Convention on Climate Change (UNFCCC), dealing with greenhouse-gas-emissions mitigation, adaptation, and finance, ratified in the year 2016. One hundred ninety-six state parties decided to establish the Paris Agreement's long-term goal as keeping the global average temperature increase to below 2°C above pre-industrial levels; and to limit the increase to 1.5°C, since this would significantly reduce the risks and effects of climate change.

To address this problem, several technologies have been extensively studied in order to reduce CO₂ emissions, such as, Carbon Capture and Storage (CCS). CCS has been considered as the most practical approach for application in existing fossil fuel power plants, especially in post-combustion processes, as well as in other industrial emitters of CO₂ (e.g. cement industry, iron and steel production), being able to long term CO₂ emissions reductions.

The most current solutions applied to reduce emissions from fossil fuels power plants are amine-based absorption processes [2]. However, this type of processes presents high values of energy penalty and cannot offer adequate performance. Then,

viable alternatives to these processes have been studied. Adsorption processes have been considered as one of the most promising technologies for CCS.

Adsorption processes, such as, Pressure Swing Adsorption and Temperature Swing Adsorption could be options, and in this context, Electrical Swing Adsorption (ESA) process emerged as a potential second-generation capture technique.

As a type of Temperature Swing Adsorption process, ESA presents an alternative mode for the regeneration of the solid adsorbent, where the regeneration is done by increasing the temperature by Joule effect, passing an electric current through the conductive adsorbent. This is an important concern because the more extensive step of the process is the desorption step, and in a CCS system, the capture stage is estimated as 60–90% of the total operating costs.

Several research works have been developed to study the viability of the ESA process for CO₂ capture.

This work constitutes a study of the viability of a new adsorbent material using Electric Swing Adsorption process for CO₂ capture from a low pressure (1 bar) and a low CO₂ content (15%) gas stream.

Figure 1.1 shows a basic scheme highlighting the focus of this work.

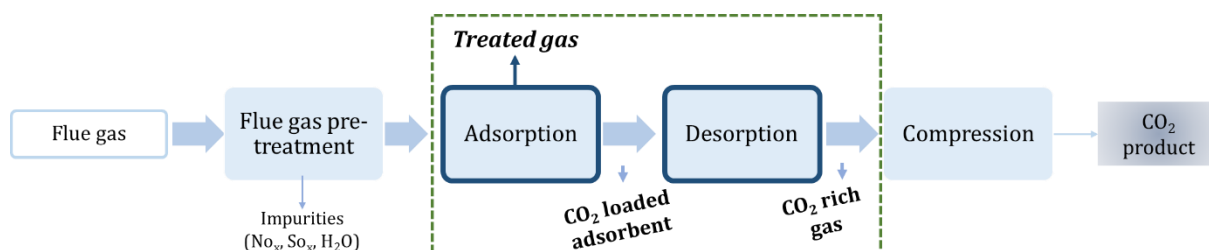


Figure 1.1 Scheme of CO₂ capture from flue gas by adsorption processes.

Previously, other works were developed by the group in this area, and it is important to clarify what had been studied before this thesis and what is the new input of this work. The work on CO₂ capture using ESA started in LSRE-LCM in 2008 by Carlos Grande [3]. Other works were published in the area [4-6], and in 2009/2010, the development of a set-up of the ESA laboratory unit was initiated. This unit was designed, built and operated during Rui Ribeiro doctoral thesis, published in 2013 [7]. During this PhD thesis, a commercial activated carbon honeycomb monolith adsorbent was studied with single

(CO₂ and N₂) breakthrough curves with electrification in the regeneration step. Even though this adsorbent presented low electrical resistivity thus suitable to be employed in ESA processes, carbon dioxide adsorption capacity revealed to be poor (2.75 mol·kg⁻¹ at 1 bar and 299 K) [7], when compared with other adsorbents, such as, some zeolites and MOFs, which present better adsorption characteristics for CO₂ capture. In addition, Rui Ribeiro studied the performance of an ESA cycle using a hypothetical composite adsorbent comprising 80% of zeolite 13X and 20% of graphite as an electric conducting binder material, in honeycomb monolith shape [7]. At the time, those materials were not commercially available, and until the moment (2019), there are still no commercial hybrid materials for this type of application with the required characteristics.

The research work involving CO₂ capture and ESA process was restarted within the group with this thesis. The aim of this work is the development of a new hybrid material suitable for ESA processes, namely in honeycomb monolith shape to provide a continuous medium for electric conduction and also to reduce the pressure drop of the CO₂ capture process. CO₂ adsorption capacity, high electrical conductivity and shaping are the main requirements of the material to be produced and represent the key challenges of this work.

Within the research group, the shaping of adsorbent materials for application in gas phase separation processes was done for the first time in this work.

1.1 OBJECTIVES AND OUTLINE

The main purpose of this work is the development of new hybrid materials for application in Electric Swing Adsorption processes for carbon dioxide capture from a typical flue gas stream of post-combustion process. The first accomplishment was to establish methods for materials production, namely, in pellet and honeycomb monolith shapes. For this, the appropriated raw materials were chosen and some methods for materials production were established. After adsorbent materials production and characterization, adsorption equilibrium isotherms were measured at different temperatures and in a low pressure range, according to the flue gases conditions. Furthermore, single and binary breakthrough experiments were done in order to study the dynamic behaviour of the adsorbents. These tests were performed with and without electrification of the bed.

The outline of the thesis is described below.

Chapter 1 presents the first introductory chapter revealing the motivation of this work.

In chapter 2, a brief state of the art is presented with a summary of all areas addressed in this work, namely in terms of technologies for CO₂ capture, types of adsorption processes and appropriate adsorbent materials for this application. In addition, the aim of producing new hybrid adsorbent materials lead to a vast research on materials shaping techniques. Moulding, extrusion and 3D-printing methods and the main works published in this area are reviewed.

In chapter 3, the methods implemented in this work are defined. A description of each method and each set-up used in the experimental part of the work is reported. Adsorbent materials development, namely by moulding, extrusion and 3D-printing process are explained. Techniques used in the adsorbents characterization are also presented.

In chapter 4, a hybrid honeycomb monolith material with 70% of zeolite 13X and 30% of activated carbon produced by Tsinghua University in China is studied. Adsorption equilibrium isotherms of CO₂ and N₂ were measured at three different temperatures at a low range of pressures. The experimental results were predicted by the multicomponent Dual-Site Langmuir model. Single and binary breakthrough curves were carried out at 298 K and 2.4 bar with different feed mixtures. A mathematical model is proposed to predict the dynamic behaviour of the adsorption bed.

In chapter 5, an extensive study with four types of pellets produced by extrusion process is done: pellets composed by 100% of activated carbon, pellets with 70% of activated carbon and 30% of zeolite 13X, pellets with 50% of activated carbon and 50% of zeolite 13X and pellets composed by 30% of activated carbon and 70% of zeolite 13X. Textural characterization by several techniques, such as, N₂ adsorption at 77 K, CO₂ at 273 K and mercury porosimetry, was performed. Topography and morphology of materials were analysed by SEM/EDS techniques. Both adsorption equilibrium and kinetic behaviour of single (CO₂) component, and kinetics of binary (CO₂/N₂) mixtures were evaluated. Breakthrough curves were carried out with and without electrification in the desorption step. All experiments were simulated by a mathematical model considering bi-disperse particles with micro and macro porosity. Furthermore, an Electric Swing Adsorption cycle with four steps was designed and simulation results were used to evaluate the performance of the developed adsorbents.

In chapter 6, the challenge of using 3D-printing as a new technology for the development of new hybrid adsorbent materials for gas separation is grabbed. The production of a honeycomb monolith material with dimensions of 30×30×43 mm, using a mixture of 70% of zeolite 13X and 30% of activated carbon is presented. Rheological properties of the ink were evaluated. Characterization of the adsorbent was extensively done, including adsorption equilibrium isotherms measurements. Single and binary breakthrough experiments with CO₂ and CO₂/N₂ were carried out. A mathematical model developed for monolith shape was adapted and applied to simulate the experimental results.

Chapter 7 summarizes the main achievements of this work and some suggestions for future work.

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2 STATE OF THE ART

An essential line of worldwide research towards a sustainable energy future is on materials and processes for carbon dioxide capture and storage. Energy from fossil fuels combustion always generates carbon dioxide release, leading to a large environmental concern with the values of CO₂ produced in the world. The increase of emissions leads to a big challenge to reduce the quantity of this gas in the atmosphere. Many areas of work are involved in solving this problem, such as process engineering, materials science, chemistry, waste management, as well as politics and public engagement [1].

To decrease this problem, green and efficient solutions have been extensively studied, as is the case of new adsorbent materials for carbon dioxide capture.

2.1 CARBON DIOXIDE CAPTURE AND TECHNOLOGIES

In pre-historic time, the energy was obtained through fire for heating and human's protection. Since the beginning of the Industrial Revolution, the power generation changed to fossil fuels sources (carbon and oil). The characteristics of this source, such as the cheap cost, the large quantity available and the large calorific power, caused its excessive use. Fossil fuels ensure most part of the worldwide electricity production, and in minor quantity other sources are employed (hydroelectric, nuclear, wind, solar and biomass). The growth of global population and industrialization are the main responsible for the progressive increase of power consumption, leading to a steady temperature rise all around the world [2]. Figure 2.1 presents this temperature increase, comparing two periods (1886 and 2012) where higher than normal temperatures are shown in red and lower than normal temperatures are shown in blue.

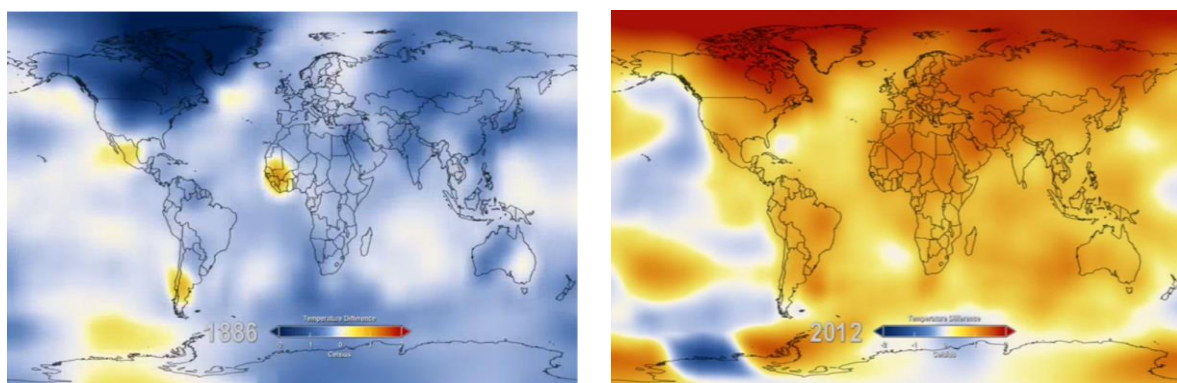


Figure 2.1. Demonstration of the global temperature anomaly registered in two periods: 1886 and 2012 [3].

Particularly since the Industrial Revolution, as said before, it is possible to observe how the planet has warmed. As a complement of Figure 2.1, Figure 2.2 demonstrates the global average temperature rise above or below 1961-1990 (the average temperature over the 1961-1990 period was used as a baseline against which yearly changes in temperature are measured) versus the time spanning between 1850 and 2017 [4].

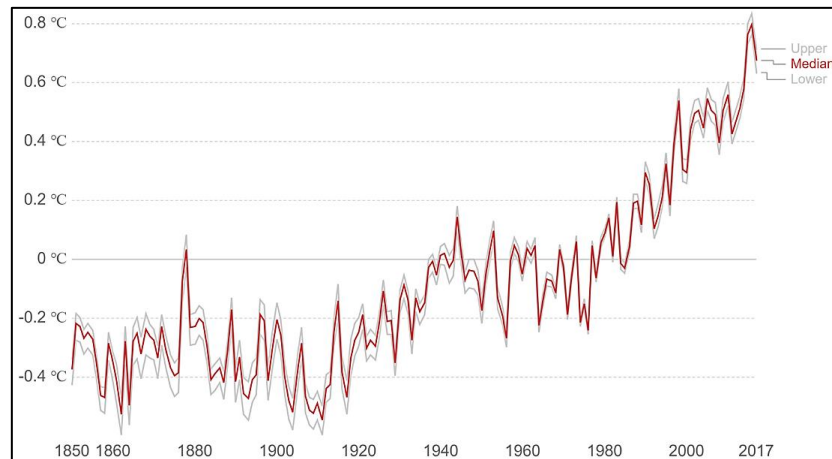


Figure 2.2. Global average land-sea temperature anomaly relative to the 1961-1990 average temperature in degrees Celsius. The red line represents the median average temperature change, and grey lines represent the upper and lower 95% confidence intervals [4].

Natural causes are also responsible for this effect, like the ice melting. However, more than 95% of global warming is caused by greenhouse gases mainly from human activities [5], as shown in Figure 2.3. The observed surface temperature variation is presented by the black bar.

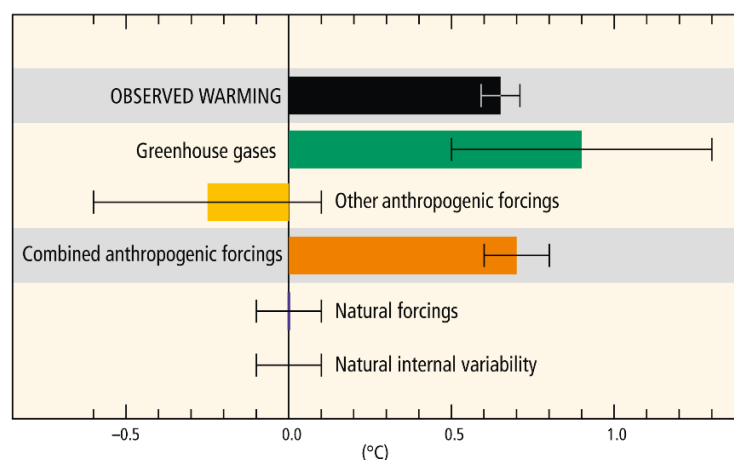


Figure 2.3. Warming trends from 1951 to 2010 from greenhouse gases, other anthropogenic forcing, natural forcing and natural variability [5].

From Figure 2.3, the greenhouse contribution in the temperature variation is clear, being responsible for about 1°C, more than other anthropogenic sources and natural variations.

The principal greenhouse gas linked to global climate change is carbon dioxide (CO₂) [2], along with the other gases, in minor quantities, such as water vapour (H₂O), methane (CH₄), nitrous oxide (N₂O) and fluorinated gases (F-gases) [6]. Figure 2.4 presents the global emissions in 2016 related with the compounds mentioned before.

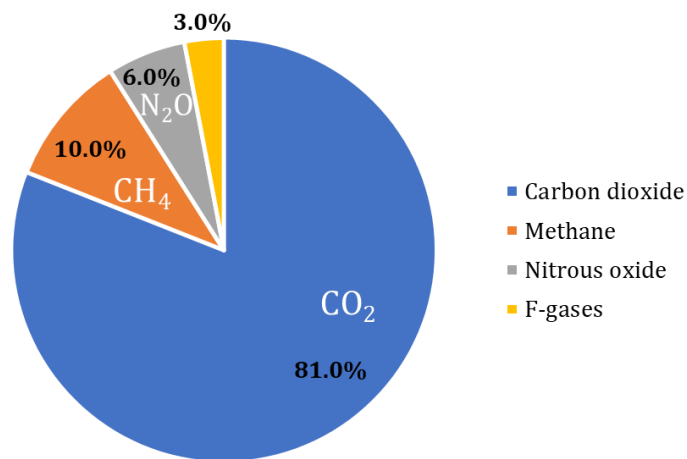


Figure 2.4. Global emissions of the principal greenhouse gases (IPCC 2016) (adapted from [7]).

It is possible to observe the high quantity of CO₂ emissions compared with other greenhouse gases. 81.0% of CO₂, followed by 10.0% of CH₄, 6.0% of N₂O, and 3.0% of F-gases, which englobe the emissions of hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and Sulphur hexafluoride (SF₆).

The energy-driven consumption of fossil fuels since the Industrial Revolution led to a rapid increase in CO₂ emissions, disrupting the global carbon cycle and causing a planetary warming impact. The climate change and global warming can have high potential ecological, physical and health impacts: extreme weather events, such as floods, droughts, storms and heatwaves; sea-level rise; disrupted water systems, among others. In this context, the Intergovernmental Panel on Climate Change (IPCC) and the United Nations Organization (ONU) established the limiting average warming to 2 degrees Celsius above pre-industrial temperatures as a target [8].

The different greenhouse gases effects on the Earth's warming can be explained by two key aspects: these gases differ from each other in their ability to be retained in the

atmosphere and in how long they stay in the atmosphere (also known as their "lifetime"). The Global Warming Potential (GWP) was developed to allow the comparison of the global warming impact of different gases. Specifically, it is a measure of how much energy the emission of one ton of a gas will absorb over a given period of time, relative to the emission of one ton of carbon dioxide [9]. By definition, CO₂ has a GWP of 1 regardless of the time period used, as for example 100-year timescale, because it is the gas being used as reference. Carbon dioxide remains in the climate system for a very long time, that is, carbon dioxide emissions cause an increase in atmospheric concentration of this gas that will last thousands of years. CH₄ is estimated to have a GWP of 28-36 over 100 years and emitted today lasts about a decade on average, which is much less time than CO₂. But CH₄ also absorbs much more energy than CO₂. The net effect of the shorter lifetime and higher absorption energy is reflected in the GWP. The methane GWP also accounts for some indirect effects, such as the fact that methane is a precursor to ozone, and ozone is itself a greenhouse gas [9].

Water vapour is another greenhouse gas with a lower GPW than CO₂ (about 5×10^{-4}). Greenhouse effect due to water vapour is small because additional vapour cannot reach the upper troposphere, and greenhouse gas warming is outweighed by an increase in reflectance from humidity-induced low cloud cover, leading to a near-zero or small cooling effect. However, the problem of water vapour is high, because when something causes a temperature increase, like CO₂ from fossil fuels, more water vapour is evaporated, and as a greenhouse gas causes a temperature increase effect [10].

Data of global warming potential factors from IPCC in 2014 showed a GWP of 23500 for SF₆, 6630 for PFC-14, 265 for N₂O, 138 for HFC-152 and 28 for CH₄ (using as a baseline GWP of CO₂ explained before, i.e., GWP for CO₂ is equal to 1).

Figure 2.5 clearly shows the CO₂ contribution to the global climate change. This gas accounts for about 81% of the global emissions of the principal greenhouse gases from human activities. The main human activity that emits CO₂ is the combustion of fossil fuels (coal, natural gas, and oil) for transportation, although certain industrial processes and land-use changes also emit CO₂. For this reason, the CO₂ concentration in the air is growing, as illustrated in Figure 2.5.

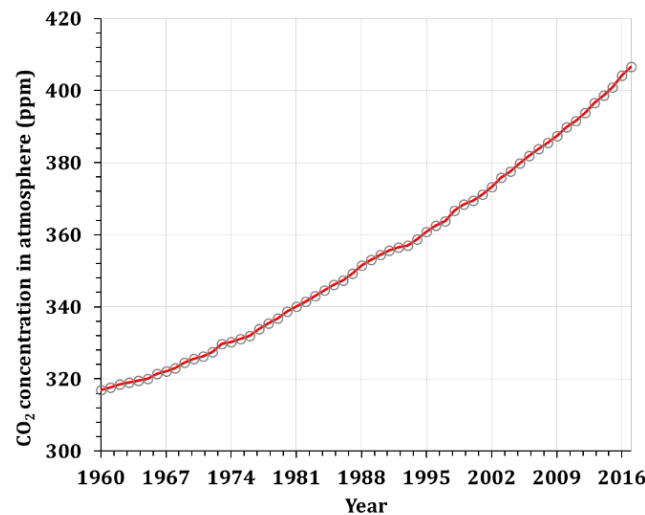


Figure 2.5. Trends in atmospheric carbon dioxide from 1960 to 2017, CO₂ concentration (ppm) measured at Manua Loa monitoring station, Hawaii [4].

The cumulative values of CO₂ emissions in the air, including the emissions through consumption of oil, gas and coal for combustion related activities, based on the IPCC data, demonstrated the high range of CO₂ emissions, depending on the country and region.

Table 2.1 shows the CO₂ emissions per world region (data of the year 2017).

Table 2.1. Distribution of CO₂ emissions per region (2017) [11].

Region	% of CO ₂ emissions
North America	18.3
Centre and South America	3.9
Total Europe	12.4
Commonwealth of Independent States (CIS)	6.6
Middle East	6.3
Africa	3.6
Asia Pacific	48.8

In 2017, the million tonnes of carbon dioxide emitted in the world was about 33500. As expected, Asia represents a high percentage of these emissions (48.8%), from which 27.6% is the responsibility of China, followed by Japan with 3.5%. Europe represents 12.4% of total emissions, being Germany the most responsible country with 2.3% of CO₂ emissions. Portugal emitted about 0.2% of the total emissions of Europe [11].

The numbers are worrisome, and it is important to understand the origin of the emissions. A recognition of this problem is the joining forces of an overwhelming majority of countries (195 nations) around the world in the Paris Agreement in December 2015. The aim of this proposal is to limit the global temperature rise to 1.5°C, i.e., 0.5°C less than the 2°C stipulated previously [12].

There is evidence that humans are responsible for most of the emissions with the burn of fossil fuels. Around 94% of CO₂ emissions arise from energy obtained from fossil fuel [13, 14], such as coal (42%), petroleum (oil) (33%) and natural gas (19%). Cement (6%) and gas flaring (1%) represents a few part of the 9% (data from 2014) [15].

The main areas responsible for global greenhouse gas emissions are energy supply (28%), agriculture (9%), industry (22%), transportation (28%), commercial and residential (11%) (data from 2016) [7].

Despite the high emissions related with the energy sector, the world will need a significant increase of energy supply in the next 20 years. It is expected that the overall energy use will increase more than two thirds between 2011 and 2035 [16].

Figure 2.6 shows the predicted need for electricity generation, until 2040.

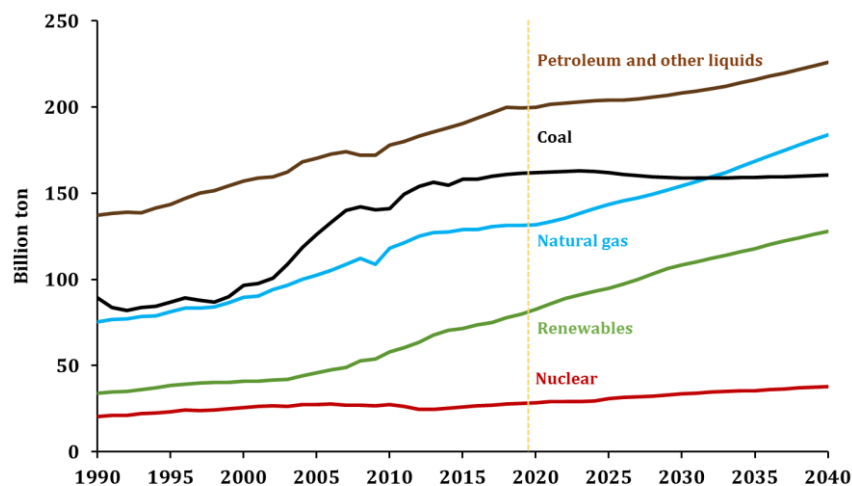


Figure 2.6. Expected world energy demand from petroleum and liquids, coal, natural gas, renewables and nuclear sectors until 2040 by IEA, International Energy Agency [8].

The development of technologies that allow the utilization of fossil fuels in a cleaner way and the construction of a green economy is increasingly urgent.

Several strategies have been studied to solve the problem. Carbon Capture and Storage technology (CCS) is one of them. Basically, CCS consists on the separation and concentration of CO₂ from power generation plants or industrial processes, its pressurization and transportation to specific locations where it should be permanently stored, as geological reservoirs [17, 18]. The economic penalty of the capture is the most important obstacle to CCS implementation. It is important that the efficiency of the CO₂ capture process is increased in the capture step of the CCS process, responsible for 60% to 80% of the overall CCS economic penalty [17]. CCS is far from the ideal solution because it does not use directly green fuels, but it is the only technology capable of maintaining the utilization of the current power plants.

This technology is being pursued, as stated by the CEO of the Global Carbon Capture Institute, after the celebration of the Paris Agreement in 2015: “it has become increasingly clear that the world will need all the technologies, mechanisms and approaches available to curb ever increasing emissions. In this past year, and for the first time in quite a long time, we have seen decisive action from a number of governments to include CCS in their armory.” [19].

Until the end of 2050, if CCS is implemented in power generation, fuel transformation and industry, it is expected that the total emissions can be reduced by approximately 19% [20]. In terms of CO₂ emissions in the European Union, if CCS is implemented at all coal-based power generation plants, the reduction would be around 60% of emissions in 2050. Of course, the total global emissions of air pollutants will be extremely reduced [21].

Nowadays, there are many technologies used and commercially available for CO₂ capture from a mixture of gases. The chosen technology depends on temperature, pressure and CO₂ concentration of the stream to be treated and on the requirements of the product purity.

In this context, the CO₂ capture technologies can be classified into three groups, pre-combustion systems, post-combustion systems and oxy-fuel or oxy-combustion processes. The first and second systems depend on whether carbon dioxide is removed, before or after a fuel is burned. In the third, pure oxygen rather than air is used for combustion [2].

2.1.1 PRE COMBUSTION PROCESS

In power plants, in oil, gas and chemical industrial processes, where CO₂ is produced, the pre-combustion CO₂ capture can be used [2]. Technologies that separate this gas from gas streams have been used for many decades. The main objective of the industries is the CO₂ removal in order to meet the required downstream product specifications, whether natural gas, hydrogen or chemicals.

Figure 2.7 shows a scheme of a pre-combustion process.

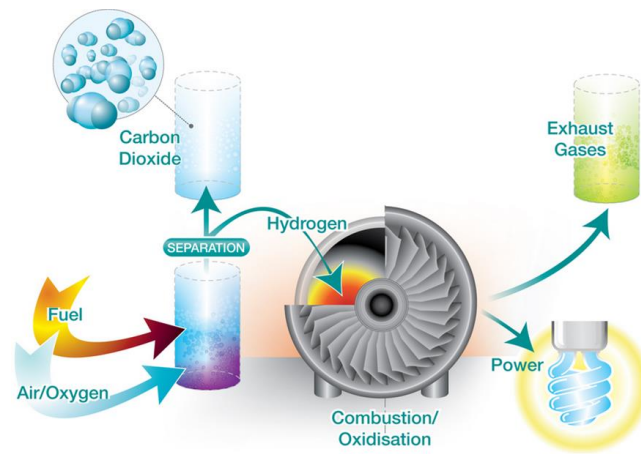


Figure 2.7. Image of pre-combustion CO₂ capture [22].

As can be seen in Figure 2.7, in pre-combustion CO₂ capture systems, the fuel source is decarbonized before combustion. More recently, in anticipation of the requirements to limit CO₂ emissions, plants design have been improved to convert the gas produced from gasification to hydrogen and CO₂ and to remove the CO₂ prior to the combustion of the hydrogen rich gas in the gas turbine [23]. The gasification or partial oxidation process combines the reacting coal with steam and oxygen at high pressure and temperature. The product is a gaseous fuel consisting mainly of carbon monoxide and hydrogen, called synthesis gas or syngas (equation 2.1).



After this, syngas is converted to more hydrogen and carbon dioxide by adding steam at lower temperature. This is the Water Gas Shift Reaction (Equation 2.2). Prior to the combustion of the hydrogen rich gas in the gas turbine, the CO₂ is captured and the concentration can be in the range of 15-60% (dry basis/% volume) and the total pressure is typically 2-7 MPa [2, 23, 24].



The Water Gas Shift Reaction is a desired route for industrial applications, most commonly in conjunction with the Fischer-Tropsch (FT) reaction to synthesize hydrocarbon fuels from syngas. The conditions used for the FT reaction lie in the range of 200–375 °C; lower temperatures for long chain alkanes and higher temperatures for shorter [25].

2.1.2 POST COMBUSTION PROCESS

Post-combustion CO₂ capture systems have been used for many decades and in this process, the CO₂ is captured from the products of burning fossil fuels or combustion exhaust gases. The flue gas passes through a liquid solvent, solid adsorbent, membrane or another medium, depending on the method/technology, allowing the separation of the CO₂ from the mixture. After that, CO₂ can be transported and stored.

Figure 2.8 presents a scheme of post-combustion process.

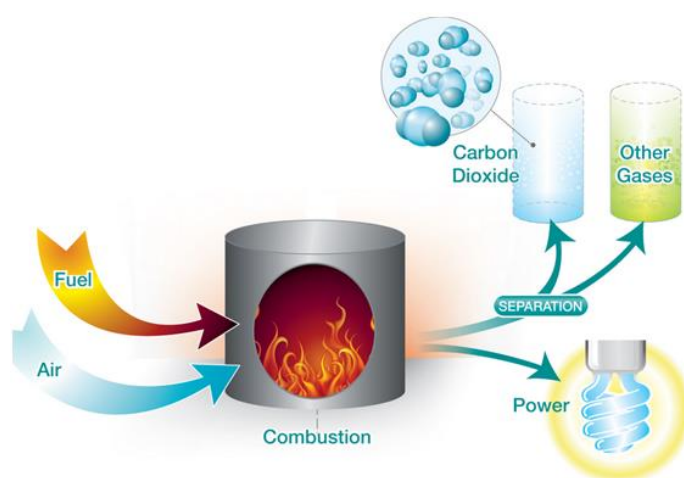


Figure 2.8. Image of post-combustion CO₂ capture [22].

The drawback of post-combustion carbon capture is the low carbon dioxide concentration in the flue gases, which leads to a relatively high energy penalty and high costs of carbon capture, while pre-combustion strives to reduce these penalties by decarbonizing the process stream rich in carbon dioxide before combustion, presenting more ability in implementation and more favourable conditions, which will significantly reduce capture costs [26].

Table 2.2 presents the comparison between the typical composition of streams to be treated by post-combustion and pre-combustion processes.

Table 2.2. Typical compositions of flue gases (by weight%) in post-combustion and in pre-combustion process [18, 27, 28].

Component	Post combustion	Pre-combustion ^(a)
CO ₂	15-16%	35.5%
H ₂ O	5-7%	0.2%
O ₂	3-4%	-
H ₂	-	61.5%
CO	20 ppm	1.1%
N ₂	70-75%	0.25%
SO _x	< 800 ppm	-
NO _x	500 ppm	3.49
H ₂ S	-	1.1%

(a) After water-gas shift reaction

Table 2.3 shows the typical operating conditions of each process.

Table 2.3. The typical operating conditions of each process [18, 27].

Conditions	Post combustion	Pre-combustion
Temperature	50-75°C	40°C
Pressure	1 bar	30 bar

2.1.3 OXY COMBUSTION PROCESS

The oxy-combustion processes were designed to remove the bulk nitrogen from the air before combustion. A combination of oxygen (95% of purity, approximately) and recycled flue gas is used for combustion of the fuel. A mixture with CO_2 and H_2O is generated by recycling the flue gas and this mixture is ready for sequestration without stripping of the CO_2 from the gas stream [29]. The flame temperature is controlled by the amount of recycled flue gas.

Figure 2.9 represents a scheme of oxy-combustion operation.

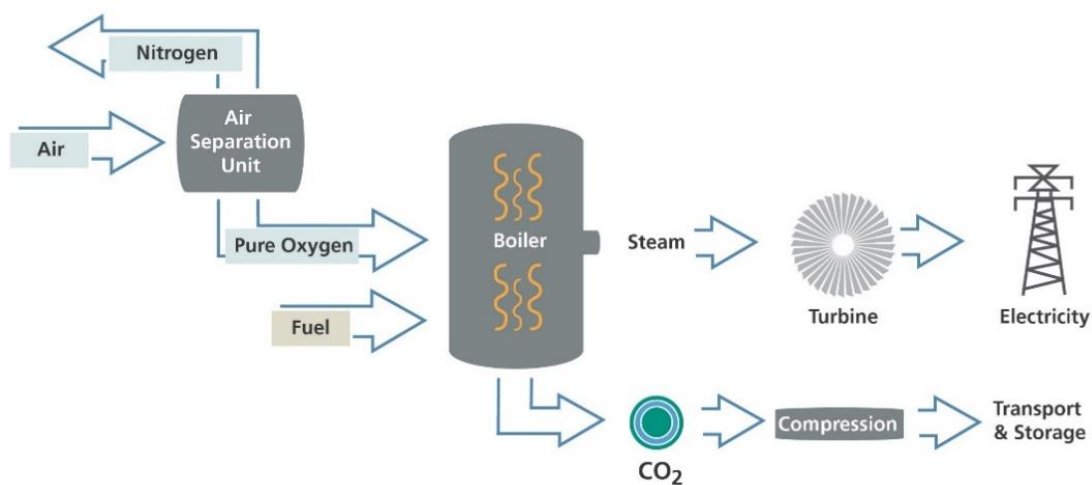


Figure 2.9. Scheme of oxy-combustion process [30].

This system was developed as an alternative to more conventional post-combustion process in coal-fired power plants. The main reason is the reduced cost of oxy-combustion when compared with post-combustion. However, although good results were obtained in laboratory scale and pilot plants, the use in commercial plants is still scarce [2].

The choice of a technology depends on the application, the resources and the aim.

2.2 CO₂ CAPTURE PROCESSES

In an industrial process, several technologies can be applied for separating or capturing CO_2 from a mixture of gases. Typically, this is a purification step and the technical process used depends on the conditions of the gas stream, such as temperature, pressure and concentration, and on the product purity required.

Figure 2.10 presents technical approaches available for CO_2 separation and capture.

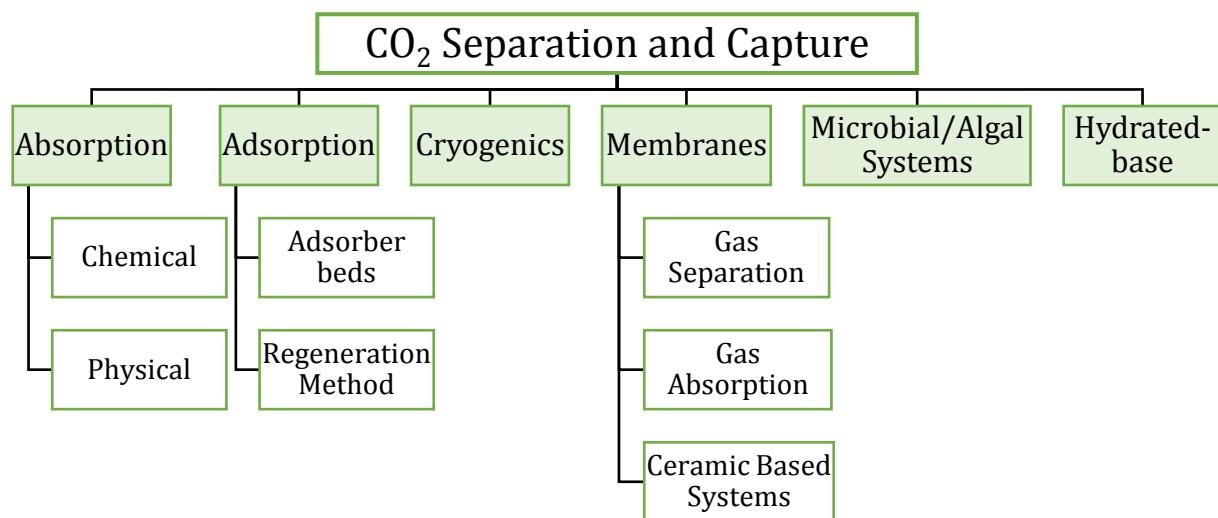


Figure 2.10. Technical options for CO₂ capture [31].

Different separation technologies can be applied to each capture type.

Actually, the most common process used to separate the CO₂ from natural gas, refinery off-gases and synthesis gas processing is absorption technology [32]. This is characterized by using a liquid/solvent that selectively absorbs CO₂ from a gas stream, and afterwards the solvent can be regenerated through a stripping or regenerative process by heating and/or depressurization [33]. Absorption processes can be chemical absorption, used both in pre-combustion or post-combustion capture, or physical absorption, mostly used in pre-combustion capture. Selexol (with dimethyl ethers of polyethylene glycol solvent), Rectisol (with methanol solvent) and Purisol (with N-Methyl-2-pyrrolidone solvent) are the most common physical processes. Typical chemical solvents scrubbing used are primary amines such as monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP), secondary amines such as diethanolamine (DEA), and ternary amines such as methyldiethanolamine (MDEA) [32, 34]. However, in this type of process, gas streams are required at high pressure. Plants for CO₂ capture with processes based on chemical absorption using MEA solvent were developed over 75 years ago to remove acidic gas impurities like H₂S and CO₂ from natural gas streams. Afterwards, the process was adapted to treat flue gas streams, and with this technology, about 85 to 95% of the CO₂ is captured, and a product stream of CO₂ can be produced with a purity higher than 99% [35].

The major challenges for CO₂ capture from flue gases are the large volumetric flow rates at atmospheric pressure with large amounts of CO₂ at low partial pressures and in the temperature range of 50-75 °C. Then, the process presents several disadvantages as high energy consumption due to the high thermal energy required, around 4.0 GJ/t of CO₂ captured [34], as well as the presence of SO_x and NO_x contaminants, and high oxygen partial pressure which hinders the implementation of amine absorption process [36]. In addition, it leads to corrosive products formation due to the thermal and oxidative degradation of the solvents. To reduce the costs involved in power plants, there are many studies about processual alternatives to reduce the operating costs. Besides the physical and chemical absorption methods discussed above, other methods could be implemented, as verified in Figure 2.10.

Cryogenic carbon capture utilizes the principle of separation based on the cooling of CO₂ to low temperature. The CO₂ is separated from the remaining gas, pressurized, and delivered at pipeline pressure. It may be a good technique, however the high compression power requirements for this method is the major disadvantage [37].

Membranes are another potential alternative to the conventional solvent absorption technology. The difference in physical and/or chemical interactions between gases and membrane materials are responsible for the CO₂ separation. The method presents many advantages, such as reduced equipment size, lower energy requirements, simplicity in the process, among others. Nevertheless, in post-combustion process, particularly in the CO₂/N₂ separation, due to the relatively low CO₂ concentration and pressure, the driving force for membranes to perform properly is weak, making their implementation difficult [38].

2.3 ADSORPTION PROCESSES

Gas separation through adsorption processes can be used in pre and post combustion capture and are promising alternative separation techniques, which are characterized by the use of solid adsorbents capable of reversibly capturing CO₂. Depending on the regeneration method, adsorption processes can be denominated as Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA), and Electrical Swing Adsorption (ESA).

In terms of industrial applications, the first commercial-scale adsorption process for CO₂ capture was developed in 2013 to be incorporated in a steam methane reformer facility for hydrogen production using vacuum-swing adsorption technology, which began full-scale operation at Air Products' facilities located on the Valero Port Arthur Refinery site in Texas, USA [39].

2.3.1 PRESSURE SWING ADSORPTION (PSA)

Pressure swing adsorption (PSA) is a cyclic adsorption process patented by Charles Skarstrom in 1960 [40], used for bulk separation and purification tasks in chemical industry due to properties such as high selectivity, high throughput and high energy efficiency. The aim of the process is to produce purified gas products, and for this, a great variety of more or less complicated PSA processes can be developed to obtain low energy requirement and low capital investment [41]. In these processes, components of a gas mixture are selectively adsorbed on a solid adsorbent at a relatively high pressure and afterwards, these components are desorbed from the solid at lower pressure. This driving force allows the recovery of the most adsorbed component from the stream without applying external heating in the desorption step [42, 43].

Pressure swing approaches could be a viable alternative to the gas absorption technology in order to reduce the costs associated with the regeneration of the solvent, such as, in the case of the conventional MEA absorption process. In terms of CO₂ capture, the energy required for this task using adsorbents could be significantly reduced when compared with amine-based processes [44].

Over the years, PSA technology has been used as a successful gas separation technique applied in a large variety of applications, like air separation [45], gas drying, and hydrogen purification [46-49], as well as in other areas like methane purification from natural or biogas [50]. This technology is commonly used, for example, in oxygen purification to produce high purity oxygen for portable devices.

PSA is a type of process more suitable for the desorption of weakly adsorbed molecules [51].

2.3.2 TEMPERATURE SWING ADSORPTION (TSA)

Temperature swing adsorption (TSA) is a process where the regeneration of the adsorbent is achieved by an increase of temperature. When adsorption occurs, for any

given partial pressure of the adsorbate in the gas phase, or concentration in the liquid phase, an increase of temperature leads to a decrease in the quantity adsorbed. By swinging the temperature from low to high, it is possible to desorb large quantities of gas. TSA has the ability to directly use the low grade thermal energy resources for adsorbent regeneration, for example, heat recover from flue gas cooling in order to offset part of the energy requirements for the capture plant [52]. These characteristics allow to apply this process in the treatment of feeds with low concentrations of adsorbates. The main challenge of this process is to reduce the regeneration step from several hours to minutes [53]. In TSA applications, the adsorbent can be regenerated by direct purge with a hot nonadsorbing gas or stream, for example, helium or nitrogen. In CO₂ capture applications, the large volume of purge gas required to heat the bed (because of the low heat capacity of gases), results in significant dilution of the extracted CO₂ product when hot nonadsorbing gas is used for regeneration. Then, the solution is heating the bed indirectly to the desired regeneration temperature using for example heating jackets, electric heating tapes, or coils wrapped around the column, or hot/cold fluid carrying tubes [52].

In order to reduce costs and to enhance the performance of TSA processes, because the adsorbate is the desired product, other methods to increase the temperature of the adsorbent and desorb the molecules have been studied, such as, direct electrical heating [54].

2.3.3 ELECTRIC SWING ADSORPTION (ESA)

Electric Swing Adsorption (ESA) process is a type of Temperature Swing Adsorption process used to regenerate the adsorbent material.

ESA processes were initially studied for treatment of effluent steams containing volatile organic compounds using a carbon adsorbent, as for example the work of Samuel Saysset [55].

In addition, ESA has been considered as a potential second-generation capture technique and there are several studies that demonstrated the viability of its application for CO₂ capture [56-59]. Different cycles and steps, as well as different materials with diverse shapes were tested and good results have been obtained.

Recently, some European projects have been developed involving the study of adsorption separation processes for CO₂ capture, such as, the LEILAC project [60], or the MATESA project with focus specifically on the study of the ESA process [61].

2.3.3.1 CONCEPTS OF ELECTRIC SWING ADSORPTION PROCESS

Electrical Swing Adsorption is a cyclic adsorption process in which the heat is generated by passing an electric current through the Joule effect. This heating is based on an electrothermal process known since 1970, when Fabuss and Dubois registered the first patent of an adsorbent directly heated by the passage of an electric current, as previously explained [54]. PSA, TSA or ESA are similar processes and they can be used for CO₂ capture applications [59, 62, 63]. The difference is in the method applied for adsorbent regeneration. When compared with TSA, ESA main advantages [64, 65] are:

- The energy expended is delivered directly to the adsorbent which implies a higher efficiency and minimization of the heat lost; moreover, the directly applied energy to the adsorbent implies that the heat transfer rate between the carrier gas and the adsorbent is not a limitation;
- Design of smaller systems due to the faster heating;
- The purge gas flow can be controlled independently of the heating rate.

The ESA process can be divided in several steps. Typically, a simpler process is constituted by three or four main steps:

- Feed - The mixture to be separated is fed to the bed at the lower temperature of the cycle. During this step, the heavier species are retained in the adsorbent material, while the light products are recovered at the column outlet;
- Electrification/Electrification with purge - Electric current is supplied to the adsorbent bed. Consequently, the temperature increases by the Joule effect action. This step should reach the end with a maximum temperature and the adsorbent is regenerated. The electric power applied to the adsorbent and the step time is defined by the process design and these considerations will define the total energy of the electrification step. This is represented by Joule's first law (equation 2.3):

$$E_{total} = \int_0^{t_{el}} P \, dt \quad 2.3$$

where t_{el} is the electrification time and P is the electric power employed ($P = VI$, and the Ohm's law is $V = IR$ where V is the electric voltage, I the electric current in the conductor and R the electric resistance). Simultaneously to the electrification, a purge gas stream can be fed to the bed usually counter-currently which helps the removal of the desorbed molecules.

- Cooling – Through this step, the temperature is decreased to the feed temperature in order to prepare the adsorbent to start a new ESA cycle. In this step, a purge gas flow is fed to the column to decrease the temperature. Typically, this is the longest step of the cycle.

Figure 2.11 shows a scheme with these steps involved in an ESA system.

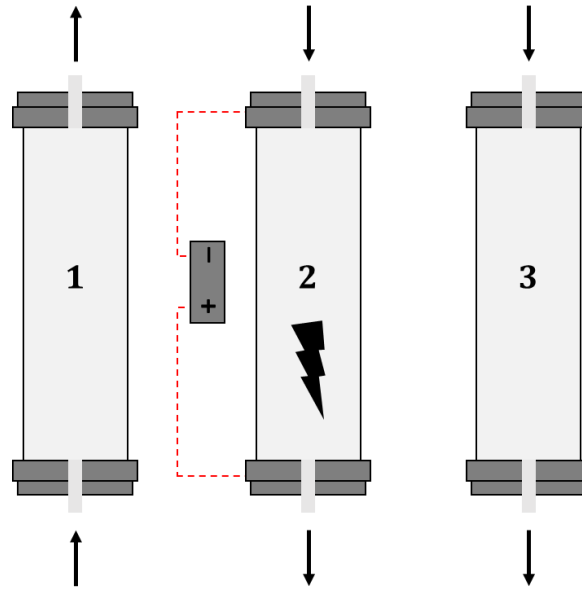


Figure 2.11. Three ESA steps: feed (1), electrification with purge (2) and cooling (3) [66].

To evaluate the performance of the cycle it is necessary to quantify the energy spent to heat the adsorbent in the electrification step. If one assumes that the energy losses and the energy needed for desorption are equal to zero, the energy spent to heat the adsorbent depends only on the mass (m_{ads}) and the heat capacity of the adsorbent (C_{pads}) and the initial and final temperature (T_i and T_f) by equation 2.4:

$$E_{ads} = m_{ads} \int_{T_i}^{T_f} C_{pads} dT \quad 2.4$$

Figure 2.12 represents the 3-step ESA cycle demonstrated in the adsorption isotherm diagram (q-T-P diagram).

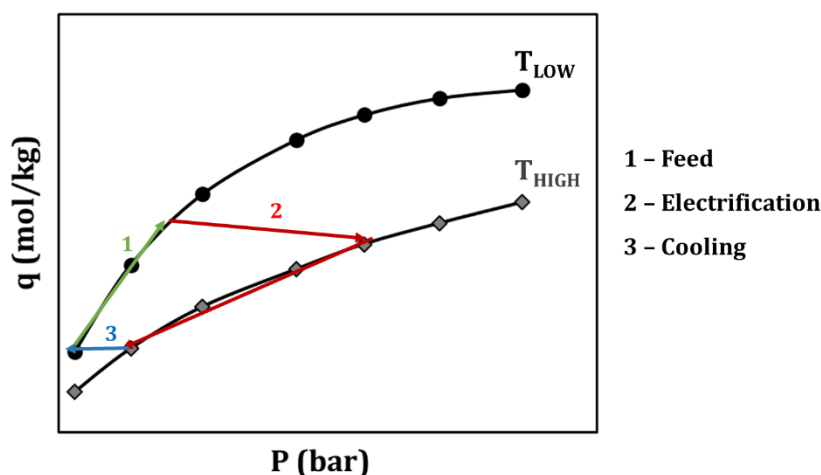


Figure 2.12. Schematic isotherms of ESA process operation of a cycle with four steps: 1 – feed (flue gas stream); 2 – electrification; 3 – cooling.

As it can be observed in Figure 2.12, the flue gas is fed to the column during the feed step at the lower temperature of the cycle. The species with stronger affinity are retained in the adsorbent surface, represented by number 1. Afterwards, the electrification step occurs with the increase of temperature (T_{Low} to T_{High}) by Joule effect. During this step, a purge gas flow can be fed to the column (flow presented counter currently in Figure 2.11), represented by number 2. In the end, the electrification is turned off and the purge is maintained until the initial temperature is reached, and the adsorbent is regenerated, represented by number 3. The system is now ready to initiate a new cycle.

Depending on the process performance needed, other cycle configurations, with more steps, could be designed and optimized, by changing the operating conditions, to reach the target values. The aimed target values are 95% of purity for the CO_2 stream with 90% of recovery, and $1 \text{ GJ} \cdot \text{ton}_{\text{CO}_2}^{-1}$ of energy consumption [67].

2.3.3.2 ELECTRIC SWING ADSORPTION PROCESS FOR CO_2 APPLICATIONS

A search on Scopus platform by “electric swing adsorption” words obtained a number of publications of 82 (until 21 May 2018). Between 2012 and 2018, i.e., in the last six years, the number of publications was 17, while in 41 years (between 1971 and 2011) the number did not exceed 65 publications. This demonstrates the growth of interest in this scientific area [68].

The first appearance of this type of process was in the work of Du Bois *et al.* (1971) [54] in which an apparatus to be used in an adsorption process to remove contaminants from a stream, as for example removal of organic vapours, such as benzene, or sulfur dioxide from an air stream, and removal of organic contaminants from a water stream, such as acetone and phenol, was described. This research was done with particles of adsorbent sufficiently conductive to be susceptible to direct heating by an electric current. Later, Gold *et al.* (1996) [69] developed an electrically conductive regeneration system for separating species of volatile organic contaminated fluid for water treatment, using an activated carbon as adsorbent.

After these studies, the number of publications in this area grew up markedly.

In the LSRE-LCM research group, the work on CO₂ capture using ESA started with the study developed in 2008 by Grande *et al.* (2008) [56].

Table 2.4 summarizes the studies published in the last 10 years by the group, related to this subject.

Table 2.4. Innovative studies about CO₂ capture with electric swing adsorption concept previously published by LSRE-LCM research group.

Electric Swing Adsorption		
Electric swing adsorption for CO ₂ removal from flue gases	Grande et al. (2008)	[56]
Electric swing adsorption as emerging CO ₂ capture technique	Grande et al. (2009)	[57]
CO ₂ Capture from NGCC Power Stations using Electric Swing Adsorption (ESA)	Grande et al. (2009)	[70]
Challenges of Electric Swing Adsorption for CO ₂ Capture	Grande et al. (2010)	[71]
Activated carbon honeycomb monolith - Zeolite 13X hybrid system to capture CO ₂ from flue gases employing Electric Swing Adsorption	Ribeiro et al. (2013)	[59]

Considering the works published, within the group and also by other researchers, it is important to highlight the challenges faced in this research area.

Recently, modelling results of a process with hybrid temperature electric swing adsorption for CO₂ capture were published by Lillia *et al.* (2018) [72]. This work presents the study of a process composed of temperature and electric swing adsorption (T/ESA) for three case studies of flue gas streams. The first case simulates the T/ESA process using as feed an exhaust stream with 12% (%molar) of CO₂, which has been chosen to validate the model against literature results. The second and third case studies consider the T/ESA application in a natural gas combined cycle (NGCC) traditional power plant, and in an NGCC plant with exhaust gas recycle (EGR). The model is simulated using a hypothetical adsorbent with 80% of 13X zeolite and 20% of activated carbon. The results presented are very promising, because T/ESA cycle estimated a costs reduction of 14.6%, while with EGR the reduction is about 11.0%, when compared with the MEA absorption plant of NGCC. However, with respect to the MEA, the energy penalty of the T/ESA is significant because of electric regeneration and fan consumptions during the heating/cooling steps of the sorbent regeneration (energetic value of electric power is 5 times higher for T/ESA than used in amine scrubbing technology).

The studies mentioned above are just a few examples of the work being developed on ESA processes. There are other relevant works on the subject, some of which are summarized in Table 2.5. Table 2.5 presents the year of the publication, the material used or considered in the model, the percentage of CO₂ in feed stream, the gas used in the desorption/regeneration/purge step, the steps used in the cycle, the values of purity, recovery and power consumption obtained, the type of work (whether it is only simulation or experimental work is also reported) and the reference.

From the list of research works presented, it is possible to observe that a great number of them is about simulation with a hypothetical or ideal adsorbent material. This is explained by the difficulty to develop a material with the ideal characteristics for ESA application, i.e., high CO₂ adsorption capacity especially at low pressures in order to be applied in the aim of the work, flue gases treatment, and to be a good electric conductor.

Table 2.5. Summary of studies and main results of works employing ESA for CO₂ capture.

Year	Material	% CO ₂	Desorption gas	Steps	Purity (%)	Recovery (%)	Power consumption (GJ/ton _{CO2})	Exp	Ref
2008	Activated carbon honeycomb monolith	4.51	Helium	1) adsorption 2) electrification desorption	-	-	7.23	Yes	[56]
2008	Activated carbon honeycomb monolith	10	Helium	1) adsorption 2) electrification (counter) 3) desorption (counter) 4) purge (counter)	23.3	92.6	-	No	[56]
2009	hypothetical 80%zeolite 13X+ 20% AC	3.5	Nitrogen	1) feed 2) rinse 3) internal rinse 4) electrification 5) depressurization 6) purge 7) purge	89.7	72.0	1.90	No	[57]
2009	70% zeolite 13X + 30% of a binder conducting material	3.5	Helium	1) feed 2) internal rinse 3) electrification 4) depressurization 5) purge	79.4	79.5	2.04	No	[70]

Year	Material	% CO ₂	Desorption gas	Steps	Purity (%)	Recovery (%)	Power consumption (GJ/ton _{CO2})	Exp	Ref
2013	18% 13X + 82% AC	8.10	Nitrogen	1) feed					
				2) internal rinse					
2013		8.10	Nitrogen	3) electrification	46.6	81.4	33.3	Yes	[59]
				4) electrification + purge					
				5) purge					
				6) cooling					
2018	30 % AC + 70% NaUSY	10	Nitrogen	1) feed					
				2) electrification					
				3) purge	44	80	2.50	No	[73]
				4) cooling					
2018	82% NH4-ZSM-5 + phenolic resin	15	Nitrogen	1) feed					
				2) electrification					
				3) purge	26	56	5.31	Yes	[74]
				4) cooling					
2018	82% NH4-ZSM-5 + phenolic resin	15	-	1) feed					
				2) electrification					
				3) purge (vacuum)	33	72	2.04	Yes	[74]
				4) cooling					
2018	80% 13X + 20% AC	12	Nitrogen	1) adsorption					
				2) recuperative pre-heating					
				3) steam heating					
				4) electrification	94.7	-	2.86	No	[72]
				5) purge (capture)					
				6) purge (recycle)					
				7) thermal recovery					
				8) cooling					

2.3.3.3 IMPORTANCE OF ADSORBENT FOR CO₂ CAPTURE WITH ESA

An important feature of adsorption processes application studies is the adsorbent material used. The importance of the preparation of new materials that combine good adsorption properties with good electrical conductivity is high, essentially for use in energy systems. Ideally, new materials should comprise a part of a conducting component, such as activated carbon, for passing electric current, and another part composed by materials with more favourable adsorption properties, like zeolites or MOFs, which do not conduct electricity and therefore, cannot be employed directly in ESA.

Besides that, the shape of adsorbent is highly important in the development of new adsorbents because they should have appropriate characteristics for application in this type of process, such as, high mechanical stability, high resistance, higher superficial adsorption area, and others.

According to this, it is important to know which materials were developed for this purpose.

A study of zeolite/electrical conductive carbon monolith suitable for ESA process is described by Masala *et al.* (2017) [75]. The CO₂ adsorption properties of a zeolite (H-ZSM-5) in powder form and in shaped monolith were compared. The monolith was developed with 78 wt.% of H-ZSM-5 and 22 wt.% of phenolic resin, which is synthesized at high temperature (800 °C) to convert the phenolic resin into a conductive carbon. A piece of adsorbent with 0.6×0.6×0.6 cm of dimension was tested. The authors present a value of resistance measured by a multimeter of 29 Ω (at a distance of 20 cm of monolith).

Zhao *et al.* (2018) [73] presented a new hybrid zeolite-carbon monolith synthesized with different compositions of zeolite NaUSY in the mixture. The slurry mixture was prepared and transferred into a glass tube to prepare the final material with cylindrical shape without channels. The final adsorbent was chosen, considering the adsorption capacity, mechanical resistance and electrical conductivity; the AC-NaUSY-70, i.e., with 70% of zeolite. The estimated resistivity was $1.18 \times 10^{-2} \Omega \cdot m$.

2.4 CO₂ ADSORBENTS

Novel adsorbent materials for CO₂ capture with specific properties can adsorb large amounts of CO₂ to be used or stored, being these materials instruments for CO₂ utilisation and storage. Adsorbents are porous solids and have a large surface area per unit mass. Each type of molecule or component creates different interactions with the surface of the

adsorbent, leading to an eventual separation [50]. There are many types of adsorbents, which could be applied to CO₂ capture by physical adsorption processes, including activated carbons, carbon fibres, zeolites, metal-organic frameworks, organic-inorganic hybrid materials and ion-exchange resins [63, 76]. The adsorbent should be chosen taking into account economic and operational criteria, which are (i) high adsorption capacity for the target gas component, i.e., CO₂, leading to a reducing of adsorbent quantity and process equipment size; (ii) high selectivity for CO₂, representing an adsorption capacity ratio between CO₂ and another component at a given flue gas composition, such as, nitrogen; (iii) fast adsorption and desorption kinetics; (iv) good physical and chemical stability during the cycles and regeneration steps; (v) be regenerable by modest pressure or temperatures leads to minimize operation energy costs. Furthermore, the adsorbent should ideally also have robust performance in the presence of moisture and other contaminants that may be in the gas stream to treat. Then, there are essential features that should be considered for a successful operation adsorbent material, such as, composition, particle size, pore size and pore connectivity.

Adsorbents with small pores are especially relevant for capturing carbon dioxide at large emission sources. These nanoporous materials can be sub-divided in three groups depending on the pore size: macroporous, when pores are higher than 50 nm, mesoporous, for pores between 2 and 50 nm of diameter, and microporous, when pores have a diameter lower than 2 nm, according to the International Union of Pure and Applied Chemistry (IUPAC) classification [77].

Over the years, two classes of microporous materials have been studied extensively, especially inorganic porous materials, as zeolites and metal-organic frameworks, and activated carbons.

2.4.1 ZEOLITES

Zeolites are microporous crystalline framework materials used in the field of gas separation and purification in the natural or synthesized form. These could be classified into groups according to common features of the aluminosilicate framework structures. The aluminium (Al) and silicate (Si) are covalent oxides that form porous structures with interconnected channels and regular cavities (cages) with molecular sizes between 0.5 and 1.2 nm [78]. The structure of zeolites consists of different SiO₄ and AlO₄ tetrahedral arrangements, in which each atom of oxygen is shared between two tetrahedra of the

structure. When compared with silicon (Si^{4+}), aluminium (Al^{3+}) has one more negative charge, leading to a framework with one negative charge for each aluminium atom. These negative charges must be balanced by exchangeable cations. In other words, for each Si^{4+} ion replaced by an Al^{3+} , the charge must be balanced by having other positive ions, such as Li^+ , Na^+ , K^+ , Ba^{2+} , Ca^{2+} , Zn^{2+} , Mg^{2+} and others. Due to these characteristics, even though zeolites share the common chemical formula of $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot m\text{H}_2\text{O}$ (where M is the exchangeable cation), there are many different zeolite structures with different pore sizes, pore openings and topologies [79-81]. The main properties, which characterize these materials, are their high degree of hydration, highly crystalline structure, high surface area, and availability for cation exchange, high adsorption capacity of gases and vapours and stability of the crystal structure. In terms of CO_2 adsorption, the highly charged species on the surface of porous solids allow high affinities when compared with other components of flue gas, i.e., CO_2 is more readily polarized than N_2 or other light gases [82]. Some intrinsic properties of each zeolite material and of each adsorbate contributes to different values of selectivity and capacity of adsorption. The main properties that could influence the zeolites performance in CO_2 adsorption capacity are basicity, polarizing power, distribution, size and number of exchangeable cations, size and shape of pores, silicon/aluminium (Si/Al) ratio, dimension of adsorbates molecules, and presence of water and other gases on the surface [83, 84].

There are many studies about CO_2 adsorption on natural and synthetic zeolites.

Synthetic faujasite zeolites have a general composition of the unit cell of $(\text{Na}_2, \text{Ca}, \text{Mg})_{29}[\text{Al}_{58}\text{Si}_{134}\text{O}_{384}] \cdot 240\text{H}_2\text{O}$ type. The secondary building units (SBU's) are double six rings and the framework density (FD) is about 12.7 nm^{-3} [85]. The unit cell contains eight cavities, each of diameter $13 \text{ \AA}$, approximately. This type of class can be divided as zeolite type X and zeolite type Y, depending on the silica to alumina ratio of their framework. In the first one, values of Si/Al ratio are between 2-3, while in the second one, this ratio is 3 or higher. [86, 87].

Zeolites type A, such as 4A and 5A, are also looked at for the assessment of their performance for CO_2 adsorption, due to some advantages presented, such as the relatively simple structure, the stability to dehydration and the capacity to adsorb small molecules.

Other zeolites, such as, ZSM-5, characterized by high acidity with the presence of H^+ cation in the structure, to compensate the excess of positive charges due to high Si/Al ratio [88], Ca-ZK5, Li-ZK-5, and Na-ZK-5, are also used for CO_2 capture [89].

In addition to the synthetic, natural zeolites have also been investigated, such as Na-mordenite [90], erionite, mordenite and clinoptilolite [91]. However, natural zeolites typically present adsorption capacities lower than synthetic materials.

Figure 2.13 presents different structures of zeolites.

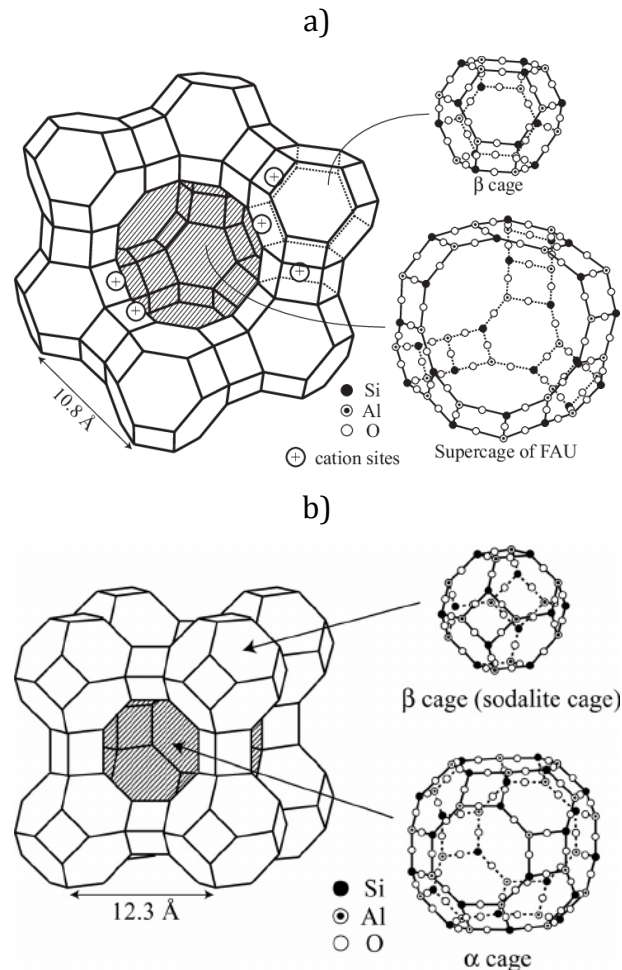


Figure 2.13. a) General structure of zeolite X and Y [92]; b) General structure of zeolite A [93].

The use of zeolites for application in adsorption processes for CO₂ capture has been reported in many works. Adsorption capacity, water stability (especially for treatment of flue gas streams), high surface areas and mechanical strength are important parameters to consider. Table 2.6 presents a summary of different values of pure CO₂ adsorption capacity for several natural and synthetic zeolites reported in the literature [94].

Table 2.6. Adsorption capacity of CO₂ for some zeolites.

Material	Property/Size	T (K)	P (bar)	q (mol·kg ⁻¹)	Ref
13X	8 × 12 mesh	298	0.1	2.05	[95]
	Pellets 0.2-0.3 mm	305	0.1	2.47	[90]
	unknown	304	0.1	3.65	[96]
13X	Extrudates 1.6 mm	298	0.1	2.49	[97]
13X	binder-free Pellets 0.2-0.3 mm	305	1.0	5.63	[98]
	binder-free Spheres	298	1.0	6.27	[90]
13X	binderless Beads 1.2-2 mm	323	1.0	4.97	[99]
LiX	binder-free Spheres 2 mm	298	1.0	6.98	[100]
NH ₄ X		298		5.31	
BaX		298		4.86	
FeX		298		3.36	
NaY	Pellets 0.2-0.3 mm	305	0.1	1.23	[90]
	unknown	303	0.1	1.77	[89]
	binder free	305	1.0	5.38	[90]
4A	unknown	298	0.1	1.25	[95]
5A	binder free beads 1.2-2 mm	305	0.1	3.38	[101]
5A	unknown	298	0.1	3.24	[102]
Na ZSM-5	unknown	297	0.1	0.92	[20]
H ZSM-5		297	0.1	0.57	
Ca-ZK-5	unknown	303	0.1	1.46	[89]
Mg-ZK-5				1.46	
K-ZK-5				2.63	
Na-ZK-5				3.10	
Li-ZK-5				3.38	
H-ZK-5				0.86	
Na-Mordenite	Pellets 0.2-0.3 mm	298	0.1	0.817	[90]
	binder free	298	1.0	2.94	
Erionite (ZAPS)	unknown	290	0.1	2.66	[91]
Mordenite (ZNT)				1.66	
Clinoptilolite (ZN-19)				1.62	
Chabazite	unknown			0.82	
Clinoptilolite	unknown	298	1.0	0.4	[96]
Clinoptilolite	unknown			0.08	

2.4.2 METAL-ORGANIC FRAMEWORKS

Metal-organic materials (MOMs) are a large class of metal moieties and organic ligands constituted by different groups of materials: discrete structures, such as, metal-organic polyhedra, spheres or nanoballs, metal-organic polygons, and polymeric structures, such as, porous coordination polymers (PCPs), metal-organic frameworks (MOFs) and hybrid inorganic-organic materials. MOMs emerged as a new family in the 1990s, and about 12 years later MOFs were described for the first time [103, 104].

MOFs are a class of hybrid solid materials with an open framework. These materials are formed by inorganic moieties or building units linked by strong coordination interactions between transition-metal cations or clusters and organic linkers [105, 106]. These moieties can be extended infinitely in one, two or three dimensions, resulting in porous materials with regular pores. The flexibility of framework, large surface areas, "tailor-made" framework functionalities, and tunable pore size are some of the key features of these materials [103], leading to more than 20000 types of MOFs [106].

MOFs can act in various applications, due to some advantages of this class of materials, such as, high surface area (the highest value, $10000 \text{ m}^2\cdot\text{g}^{-1}$), controllable pore size (from a few Angstroms to $98 \text{ \AA}$), and low density (the lowest value, $0.13 \text{ g}\cdot\text{cm}^{-3}$). Different areas, such as gas separation and storage, reaction containers to selectively catalyse some organic reactions, stationary phase in chromatography, sensors, and others, are already known for the utilization of MOFs.

In order to extend these applications, the combinations of MOFs and other functional materials have been studied, improving the MOF performance. In addition to individual functions of the MOFs and functional materials, the merge provides multifunctionality as a whole and generates new physical and chemical properties that are not present in the individual components [106], for example, the inclusion of graphene, carbon nanotubes (CNTs), metal nanoparticles and nanorods, metal oxides, complexes, and even enzymes, among others.

Figure 2.14 presents a schematic illustration of metal-organic framework materials, composites and derivatives.

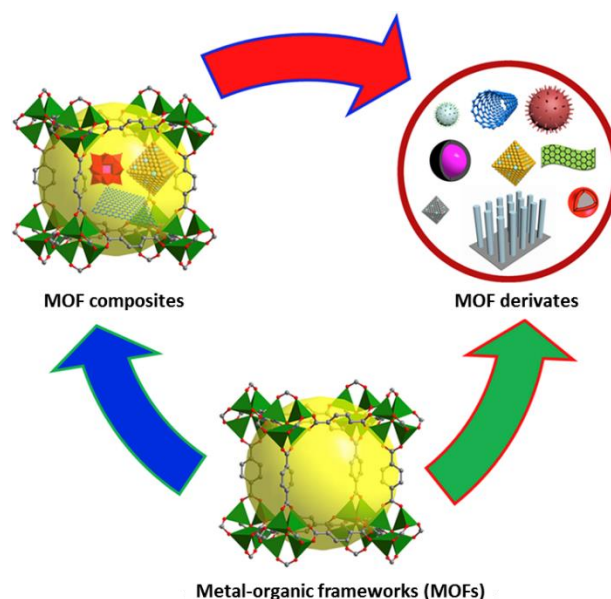


Figure 2.14. Schematic illustration of MOFs, MOF composites, and MOF derivatives as well as their conversions [106].

The high CO₂ adsorption capacity of some MOF materials is a reason for their use. However, in humid environments, the stability of the MOF material can be a decisive factor in the ability to its use as an adsorbent. Since 2012, water adsorption isotherm studies have also been measured, such as in materials like Cu-BTC (HKUST-1), MIL-100, MIL-101, MIL-53, MOF-74/CPO-27, UiO-66, and ZIF-8 [107]. With these recent advances in water stability tests, the application of MOFs can expand. Combination of high capacity with high selectivity in the presence of humidity are future directions and challenges of these materials.

Table 2.7 presents a summary of CO₂ adsorption capacity of diverse powders of MOFs.

Table 2.7. Adsorption capacity of CO₂ for some MOFs at 298 K.

Material	P (bar)	q (mol·kg ⁻¹)	Ref
HKUST-1	0.1	0.60	[108]
UMCM-150(N)2	0.1	0.29	[108]
MIL-47	0.1	0.18	[108]
ZIF-8	0.1	0.12	[108]
IRMOF-1	0.1	0.07	[108]
IRMOF-11	1.0	1.77	[109]
MOF-505	1.0	3.31	[109]
Cu ₃ (BTC) ₂	1.0	4.11	[109]
IRMOF-3	1.0	0.97	[109]
IRMOF-6	1.0	0.65	[109]
MOF-74	1.0	4.84	[109]
MOF-74(Ni)	1.1	4.06	[110]
MOF-74(Co)	1.1	3.67	[110]
MOF-177	1.0	3.28	[111]
MOF-5	1.0	3.11	[111]

2.4.3 ACTIVATED CARBONS

The exact year that activated carbon or charcoal began to be used as adsorbent is unknown in history. However, there is evidence of its usage and importance throughout history, from the ancient world to the modern era.

Activated carbons (ACs) are amorphous porous forms of carbon and have great interest as CO₂ adsorbents. These materials can be prepared by pyrolysis of various sources of carbon such as coal, coke pitch, wood and biomass [76]. Depending on the raw materials, several types of activated carbon can be obtained, and consequently the differences in graphite structure and surface functional groups cause different adsorption capacities of the materials [112]. The main advantages of activated carbons are the wide availability, low cost, high thermal stability, high surface area (BET areas larger than 2000 m²·g⁻¹) and micropore volume (maximum between 1.3 and 1.7 cm³·g⁻¹). In addition,

the hydrophobicity of carbons surface make them materials stable in the presence of water vapour, which is an advantage for some applications [113].

ACs have been studied experimentally and theoretically for a long time and several commercial applications have been found [114]. ACs in different forms are applied in different applications, such as the ones explained in Table 2.8:

Table 2.8. Different forms of activated carbon raw materials.

Forms of activated carbon		
Granular Activated Carbon (GAC)		• irregular shaped particles • sizes ranging from 0.2 to 5 mm • used in both liquid and gas phase applications
Powder Activated Carbon (PAC)		• pulverised carbon • size predominantly less than 0.18 mm (US Mesh 80) • mainly used in liquid phase applications and for flue gas treatment
Extruded Activated Carbon (EAC)		• extruded and cylindrical shaped • diameters from 0.8 to 5 mm • mainly used for gas phase applications due to low pressure drop, high mechanical strength and low dust content
Charcoal Activated Carbon Cloth (ACC)		• special forms such as cloths and fibres

Table 2.9 presents a summary of CO₂ adsorption capacity for some activated carbons.

Table 2.9. Adsorption capacity of CO₂ for some powders of activated carbon (AC).

Material	T (K)	P (bar)	q (mol·kg ⁻¹)	Ref
G08H	301	0.1	0.26	[115]
MSC-30	301	0.1	0.38	[115]
CaO Doped-MSC-30	301	0.1	0.19	[116]
MgO doped-MSC-30	301	0.1	0.25	[116]
CaO-MgO doped-MSC-30	301	0.1	0.39	[116]
Maxsorb-III	300	1.0	2.09	[117]
Norit, R2030	298	1.0	2.20	[118]
BPL-AC	298	1.0	0.28	[119]

2.5 SHAPING OF ADSORBENTS

The shaping of adsorbents is an important aspect of the adsorption processes. In the conventional industrial processes, gas separation is usually performed using adsorbents in the form of beads or granules, such as, the separation of flue gas from a coal-based power plant. However, depending on the application, some aspects should be considered in the shaping of an adsorbent. External and internal mass transfer resistances and pressure drop drawbacks associated with packed beds impose limitations in operating the processes at optimum conditions, in terms of energy consumption and overall efficiency. To reduce these problems, shaping of solid adsorbents through appropriate choice of materials, size and shape, by applying a suitable manufacturing technique, are being investigated, such as, alternative adsorbent geometries in order to satisfy the process requirements. Some properties that this novel adsorbents should have are high volume working capacity (high loading per unit), low voidage for minimizing the size of adsorbent, high mass transfer kinetics, among others [120].

These questions have been extensively studied in diverse research works. Diverse techniques of shaping adsorbents are currently used, especially to create particles or beads.

Pelleting is a high-pressure agglomeration technique to produce pellets or particles, usually short cylinders with high shape accuracy. Granulation is a type of process where the size enlargement is done by wet tumbling-growth agglomeration. A cohesive liquid is

sprayed onto the adsorbent powder such that the wetted particles stick together [121]. The extrusion process is the most widely used technique for the shaping of materials. The concept consists in passing a highly filled suspension or paste through a profiled die that determines the shape of the green body.

Another type of shaped materials is monoliths. These adsorbents can be of various shapes like cylinders, discs, and others. Due to the long channels contained in their structure, honeycomb monoliths can have higher surface areas when compared with a conventional bed of pellets or extrudates.

2.5.1 HONEYCOMB MONOLITHS ADSORBENTS

The preparation and evaluation of monoliths in adsorption systems were widely investigated since the 1970s [122-125].

Honeycomb monoliths adsorbents are structured supports with body diameters of 1.0-50 cm and lengths of few centimetres to meters. These materials possess parallel channels with a variety of cross-sectional shapes, such as, square, triangular, hexagonal or sinusoidal, being the square channels mostly used [120]. The geometry of honeycomb monolithic structures is characterized completely by four parameters: the shape of the channels or cells, the channel size, the wall thickness and cell density (number of cells per unit surface area). Cell or channel densities are usually in the range between 1.4 and 93 cells·cm⁻².

Regarding the shape of the adsorbent, a monolith is highly desirable due to the high mechanical stability, improving the performance in industrial application, including catalytic combustion, biochemical and electrochemical reactors, automotive catalytic converters, high resistance toward abrasion/attrition, higher volume to surface ratio, homogeneous power distribution, efficient mass and heat transfer, and lower pressure drop, when exposed to high volumetric gas flow rates, implying lower operating costs in a plant in which a large volume of gas is to be treated [120, 126]. These advantages make this shape ideal, especially due to the low pressure drop, a major restriction of post-combustion CO₂ capture processes.

Honeycomb monoliths can be distinguished in two different types – coated or integral, depending on the preparation method. Coated honeycomb monoliths have a thin layer of other substance, generally called the wash coated layer, that cover the inner surface of the channels, improving the internal surface area. Generally, a honeycomb

monolith with good mechanical properties is used to coat with a substance. Integral honeycomb monoliths should comprise good mechanical properties and should have other attractive characteristics, such as, high surface area, adequate porosity and surface chemistry more appropriate to the required use. The preparation of these materials needs a great effort to find the adequate conditions that conduct to these properties.

To study the production of new adsorbent materials, it is important to consider the raw materials used, the techniques of production, the final structure and the application, in order to define the best adsorbent.

Figure 2.15 shows different types of honeycomb monoliths structures.



Figure 2.15. Types of honeycomb monoliths structures ([127-129], respectively from left to right).

2.5.2 PROCESSES OF MONOLITHS SHAPING

The importance of having an adsorbent material in shaped form for an adsorption process has become evident. Then, the study of materials preparation for application in adsorption processes is constantly growing. In this context, a review of adsorbent material shaping, the main techniques used, and the principal works published is important. Powder shaping area involves a large number of processes, such as, dry pressing or molding, spray drying, tape casting, extrusion, coating and more recently, 3D-printing [130].

These known techniques to produce adsorbent structures are used, in particular, to produce monoliths. Particularly in CO₂ separation, there are a large number of patents of monolith structures with activated carbon, zeolites and MOFs materials [131-134].

Coated materials are largely used for many different applications. Darunte *et al.* (2017) [135] studied the potential use of an amine-functionalized metal organic

framework supported on a structured monolith for CO₂ capture, which demonstrated high CO₂ adsorption capacity with a stable performance over multiple cycles.

Hosseini *et al.* (2015) [136] presented a work of a modified carbon-coated monolith for CO₂ recovery from He/CO₂ mixtures. The monolith was prepared by dip-coating method and was treated with two different alkaline solutions, NH₃ and KOH. The modified monolith demonstrated an improvement of CO₂ uptake, when compared with the unmodified material. However, the problems associated with the coating/wash coating process, such as, blockage of channels or pores, poor adhesion, and cracking during drying due to the capillary forces, are big [137].

Akhtar *et al.* (2014) [138] presented the production of cylindrical aluminophosphate tablets (AlPO₄-17 and AlPO₄-53) in a graphite die of 12 mm in diameter by pulsed current processing (PCP) for CO₂ capture. The adsorptive properties, mechanical strength, CO₂ capacity and low energy cost for regeneration render them candidate-structured adsorbents for CO₂ capture from flue gas mixtures.

Akhtar *et al.* (2012) [139] developed three cylindrical structures applying high pressure to the powder body during heating and holding cycle to form consolidated materials without binders. Adsorption, structural and mechanical properties were studied. The obtained monoliths showed a high capacity to adsorb CO₂, high CO₂/N₂ selectivity and a rapid uptake of CO₂, displaying a good cyclic performance, regeneration conditions and mechanical strength promising for rapid swing adsorption.

To study the production of integral monoliths, a vast research about processes of monoliths production is very important.

2.5.2.1 MOULDING

The manufacture of simple structures with cylindrical shape without channels or rectangular block of carbon composites has been previously attempted [140, 141].

Burchell *et al.* (1997) [141] presented the synthesis of a carbon fiber composite molecular sieve (CFCMS). The slurry, prepared by mixing carbon fibers, powdered phenolic resin and water, was transferred to a moulding tank. The water is then drawn through a porous screen under vacuum, resulting in a dried piece. The formed composite is cured and carbonized at 650 °C in an inert gas environment.

Another work with this type of preparation was reported by Shams *et al.* (2007) [142]. A NaA zeolite powder was mixed with kaolin, carboxymethylcellulose and water

and stirred with a spatula, preparing the slurry. The paste formed was passed through a homemade extruder, applying pressure, to form a thin structure (tablet). After a drying step, the material is activated at high temperatures in an inert ambient.

Based on some published works about this type of materials preparation procedure [142-145], a scheme with the principal steps of the production was done.

Figure 2.16 shows a schematic production route of monoliths.

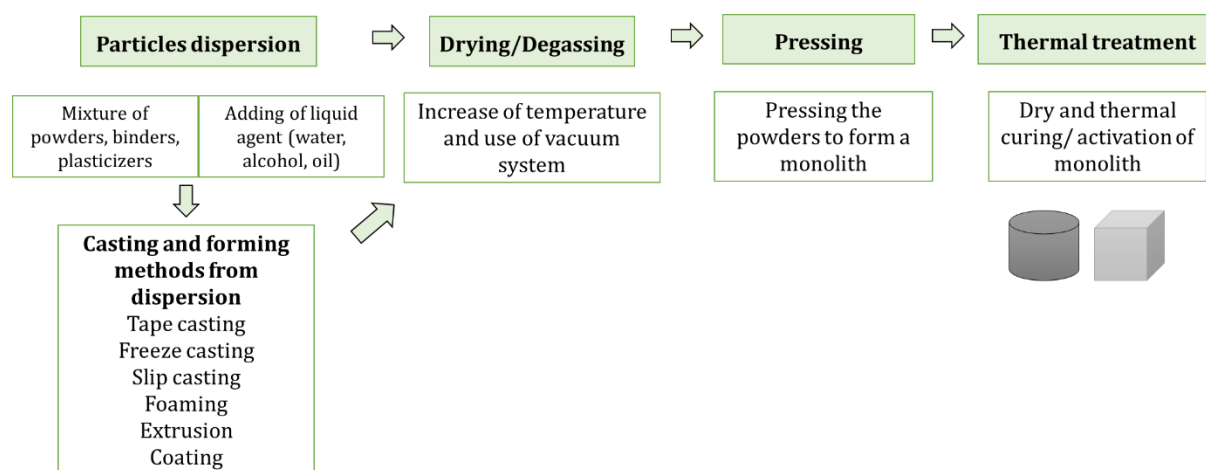


Figure 2.16. Scheme of principal processing steps and shaping of production of porous adsorbents.

Briefly, the process is based on mixing the stable dispersions of raw materials, such as, zeolites, activated carbon, or MOFs powders, with suitable agents, such as binders, plasticizers or dispersants liquids, to form a paste with ideal rheological properties. The final paste can be formed by different methods, such as, tape casting, slip casting, filtration, or other. The formed dispersion is dried and degassed to remove the excess of liquid or solvent used. After that, a step at high pressure occurs to form a green piece of monolith, which is treated and afterwards activated in an inert ambient at high temperatures. The use of ligands/binders is prejudicial for the adsorption capacity of the materials, and in the case of structured adsorbents, fabrication without binder (binder free) is possible, due to the capacity of moulding of the raw materials. Pulsed current processing (PCP) method can be used [146].

In Chapter 3 a detailed description of the processes used in this work, with the information of all materials, such as raw adsorbent materials, binders and solvents, is given.

2.5.2.2 EXTRUSION

The research about monoliths production demonstrated that, practically, all monoliths are produced by extrusion process.

The scheme showed in Figure 2.17 presents the main steps of this type of processing of porous powders.

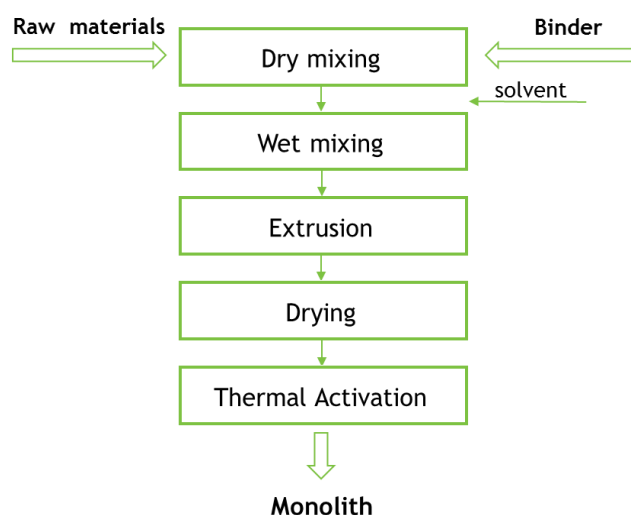


Figure 2.17. Preparation steps of extrusion process.

The extrusion process involves the mixture between powders with inorganic and organic additives, the shaping of powders into the desired form by extrusion process and the removal of part of the additives by drying and creating a mechanically robust structure by thermal treatment. During the mixing and extrusion steps, a type of kneading machine is usually employed to prepare the wet mixture. Afterwards, the mixture passes through a screw, and is then conducted to the die, forming the extruded material. The rheological properties of the prepared paste are very important to allow the extrusion through the die and to have enough cohesion to form the surface and bulk without defects.

Aranzabal *et al.* (2010) [147] reported a successfully produced H-ZSM-5 zeolite monolith by extrusion process using a Brabender extruder. The authors refer that the method used avoids the difficulties to fix the crystalline zeolite material to the monolithic support and also allows to get an uniform synthesis of zeolite along the whole monolith. A Ti_3AlC_2 honeycomb ceramic monolith with good mechanical properties and electrical conductivity was developed by Fang *et al.* (2015) [148], being a promising material of the conducting honeycomb monoliths for industrial applications, such as, treatment of

exhaust gases emitted from vehicles containing harmful components (CO, hydrocarbons and nitrogen oxides). Lim *et al.* (2010) [149] presented an easy preparation method for production of activated carbon honeycomb monolith with a mixture between adsorbent material, low-density polyethylene as organic polymer and organic lubricant. The mixture was extruded with a square shape with 16 cm² and 256 cells. The potential uses of these extruded monoliths as adsorbents for removal of volatile organic compounds (VOCs) were extensively studied. Chafik *et al.* (2009) [150] presented a work on honeycomb shaped monoliths preparation with natural clay samples (FERA and TEFA, obtained from different deposits located in the north of Morocco), without the use of chemicals, binders or plasticizers. The materials were tested for VOCs adsorption.

In this type of processes, the consequences and the possible effects of binders or additives used are important. Depending on the production process and the final characteristics required, additives and the use of different combinations allowed for the improvement of the rheological properties of the paste during the kneading operation. The addition of binder can help the formation of the adsorbent structure, provides corrosion resistance and protects the raw materials from external damage. In addition, binder helps to keep the particles in a compressed state [13].

Figure 2.18 shows the scheme of bonding process of porous particles and binders.

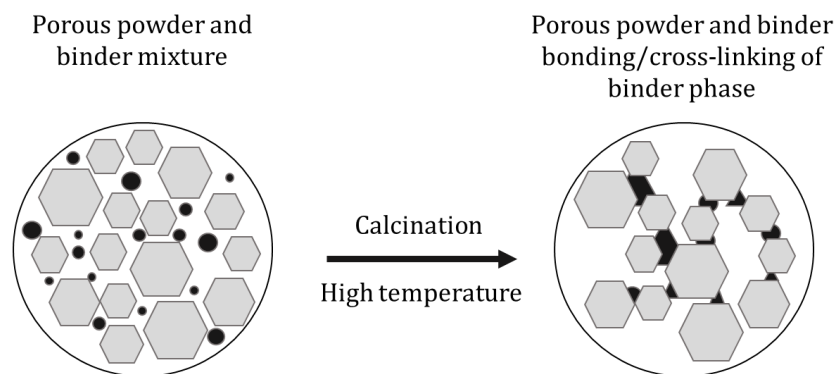


Figure 2.18. Scheme of the bonding process between porous powders materials (adapted from Akhtar *et al.* (2014) [130]).

2.5.2.3 3D-PRINTING

Since the XX century, the development of 3D-printing was initiated by a set of concepts, such as three-dimensional printing, topography and photo sculpture. In 1980, Dr. Kodama developed the first 3D printer prototype which used a layer by layer technique with photosensitive resin polymerised by a UV light, for manufacturing, a predecessor to Stereolithography [151, 152]. This development conducted to the first patent of a real 3D commercial printer by 3D Systems enterprise in 1987-1988 [153, 154].

Hereafter, the knowledge did not stop anymore and in 1988, a new patent was published for another 3D-printing technique, selective laser sintering (SLS) in which powder grains are fused together locally by a laser [155]. At the same time, Scott Crump developed the Fused Deposition Modelling (FDM) as the third 3D-printing technique [156, 157].

In the 90s occurred the emergence of 3D printers' equipment, techniques and CAD tools with added contribution for this area. Apart from the plastics, 3D printers began to use heat-resistant polymers and metal alloys, allowing rapid tooling applications. This technological advance brought many advantages especially in the injection moulding and die casting manufacturing industries, due to the high costs and lengthy fabrication processes that were significantly reduced [158].

In the late 2000s, the quality of 3D printings was already high as well as with high precision. This, coupled with costs decrease, allowed its use in mass production of final products [158, 159].

Figure 2.19 shows the major marks of 3D-printing technologies in recent years.

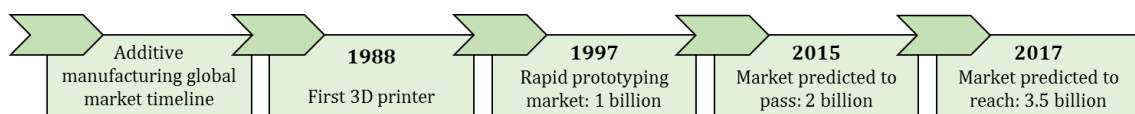


Figure 2.19. Grow of additive manufacturing industry (adapted from Bandyopadhyay *et al.* (2016) [160]).

3D-printing technology is based on two clear concepts, which are the definition of the desired technology with the aid of a digital software and the fabrication through layer-by-layer deposition until the piece is completed [154, 159].

There are many designations for additive manufacturing and names are usually based on materials and processes for each type of printing. Three of the most commonly

used names are rapid prototyping (RP), term that was further popularized because it represents the aim of the technology creation, i.e., developed in order to substitute the prototyping, long and expensive tasks of the product development; stereolithography (SL), term used to define the name of the first commercial equipment available by 3D Systems enterprise; 3D-Printing, term used to define the new technology by researchers [154].

Due to the lucrative value and abilities of this technology, the market has been expanding very quickly [160]. Over the years, prototypes, functional and polymeric materials can be made to perform in a large variety of environments. As one might expect, this innovation has gained even more importance in diverse industries and areas of research, such as chemical engineering.

Especially in recent years, this growth can be seen in the number of published articles.

The Scopus platform [161] was used to search the works published in this area, and the words were searched in titles, abstracts and keywords of publications. Since 1988, the number of publications of 3D-printing is about 14000 (6 February 2019). Accessing this website, an advanced search using keywords in titles and abstracts was carried out. A search of title and keywords of articles with “3D-printing” word was conducted using some filters; by area of publication – chemical engineering, the number of articles is 1197 (6 February 2019), 1172 are since 2010. If the search is restricted to include CO₂ or monolith in keywords, the number decreases to 9 and 14 publications, respectively. These numbers demonstrated that the number of articles involved in this topic of investigation, such as, monoliths for CO₂ capture, is negligible.

Figure 2.20 shows a strong growth of additive manufacturing industry since 2009.

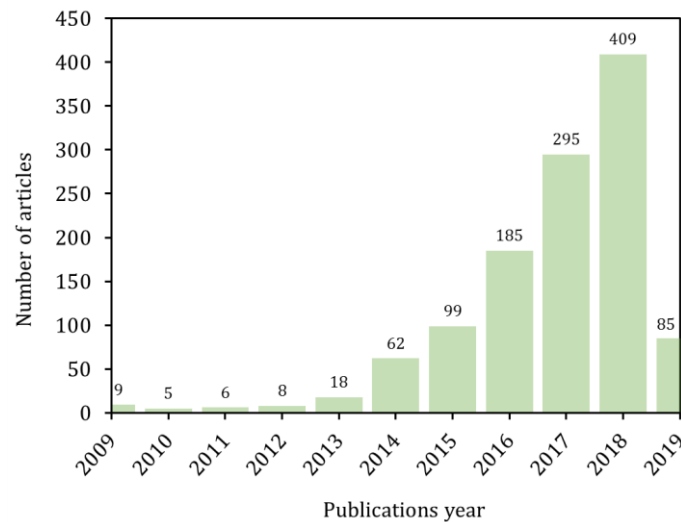


Figure 2.20. Number of articles published by year in chemical engineering of 3D-printing research area since 2009.

3D-printing technology could be applied in some areas, and depending on the final objective, by different methods.

However, additive manufacturing presents advantages and disadvantages. Table 2.10 shows a simple collection of the main points [160, 162].

Table 2.10. Principal advantages and disadvantages of 3D-printing process.

Advantages	Disadvantages
<u>Design freedom with materials saving</u> Additive manufacturing can make any geometry with no restrictions, and less waste of raw materials is created	<u>Material and size restrictions</u> Limited versatility among different 3D printers, and the use of liquid polymer or a powder means that large objects cannot be produced
<u>Versatility</u> Easy to change design and complexity of parts	<u>Presence of imperfections</u> Pieces can have a rough and ribbed surface finish
<u>Flexibility</u> Additive manufacturing has no tooling constraints in production parts and, in production, machines do not require costly setups	<u>Higher costs</u> Investment can be high, as well as the accessories, resins and materials needed for operation

2.5.2.4 ADDITIVE MANUFACTURING – PRINCIPLES AND TECHNIQUES

Additive manufacturing, defined as the fabrication of products with layer by layer technique, is a technology where human intervention is virtually null [159]. The fabrication is based on a three-dimensional geometric model created and interpreted through a specific software.

The concept of 3D-printing follows several steps until the final product is obtained. Initially, the idea is the starting point. After that, the design is created using an appropriated 3D modelling program. At this point, the archive should be transferred to the equipment by, for example, a pen drive or a direct connection with a computer. The equipment is able to read a computer specific file format, like STL or IGES. For each 3D printer it is possible to choose the material to print the model, because it is possible to change the type of raw material, such as polymer, resin, ceramics or composite pastes, colour of filaments, and others, whichever the final aim. When everything is prepared, one can start to print the piece and the operator has only to observe. When the process is concluded, the piece should be removed carefully from the plate in order not to break [163, 164].

Figure 2.21 shows a scheme with some steps involved in 3D-printing process.

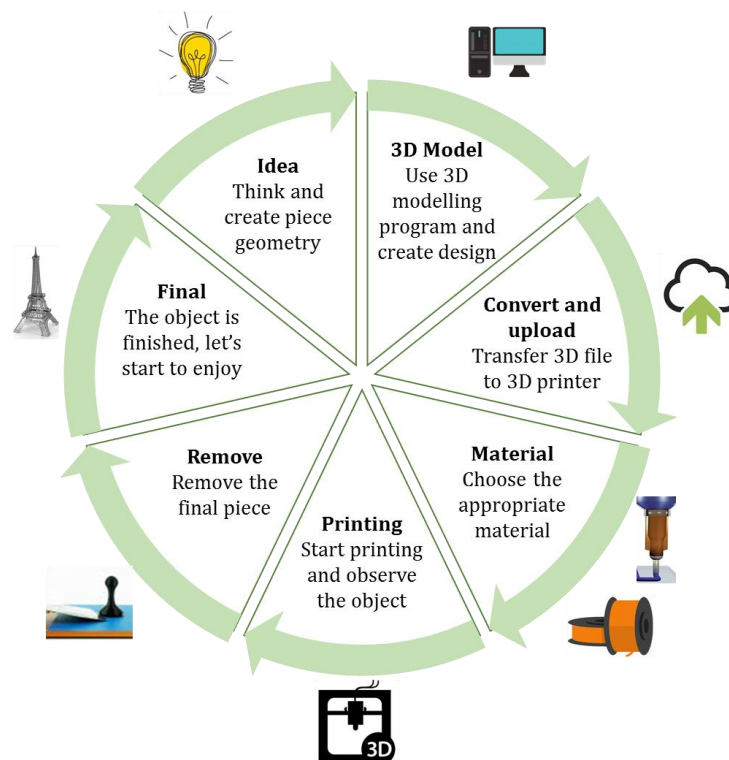


Figure 2.21. Scheme of various steps involved in a 3D-printing processing.

All printing methods are explored according to the raw materials available and the final objective. Generally, the different techniques can be classified into three groups: a liquid or a paste formed by powders, transferred to the substrate without direct contact with the surface, or a solid in contact with a stamp or writing head with a substrate [162, 165].

There are some methods for 3D-printing and diverse designations. The most widely known techniques are expressed in Figure 2.22 and a brief description of each of them is presented below.

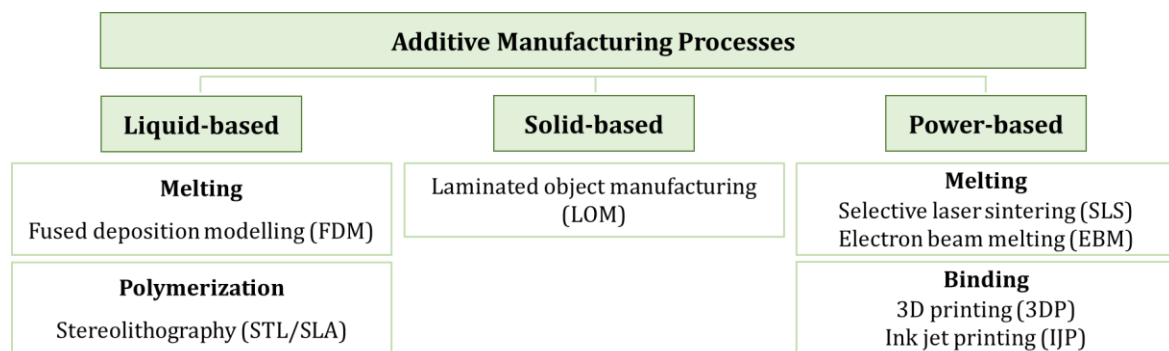


Figure 2.22. Overview of various additive manufacturing processes (adapted from Srivatsan *et al.* (2015) [162]).

Fused Deposition Modelling (FDM) or *Fused Layer Modelling* (FLM) technique uses a polymer in filament/plastic form that is compressed, heated at high temperatures to locally melt and extrude through a nozzle, being deposited layer by layer from the bottom up in order to fill the outline in the platform [166, 167], enabling the adhesion by solidification of the extrudate during contact with the already built material. This methodology allows the use of a large variety of polymers, in solid form. The employed polymers are thermoplastics, such as, polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and polyphenylsulfone (PPSU). Due to the easy handling, the low cost, and the use of single-nozzle extrusion, this technique enables the printing of relatively large pieces within a relatively short time, making this technique one of the most popular in the market [164, 168].

Stereolithography (STL) or *Photopolymerization* is the oldest process and still the most accurate process. The system works with a liquid photopolymer surface crossed by a laser beam, hardening with the exposure to the direct ultraviolet radiation. Then, the

liquid mixture of monomers is converted into cross-linked macromolecules, plastics [164]. The procedure occurs until one layer is completed, and after this, the platform is lowered and the procedure is restarted [164]. STL technology presents some advantages, among which, the two most noticeable are accuracy and surface finish [163].

Laminated object manufacturing (LOM) is a technique used to print diverse materials such as, monolithic ceramics, ceramic and polymer matrix composites, and others. In this process, a continuous sheet of material, plastic, metal or paper, which is drawn across a build platform by a system of feed rollers, is fused or laminated together using heat and pressure then it is cut into the desired shape with a computer-controlled laser or blade [169]. After one layer is printed, the build platform is lowered, according to the thickness defined. This process is repeated until the entire object has been formed [170].

Selective Laser Sintering (SLS) or *Selective Laser Melting* (SLM) technique consists in a high potential laser beam on a surface with a powder, sintering and creating a solid layer. Successive layers of powder are deposited and melted, bind to the layer deposited below and solidify [167]. The most common printable materials are metals and alloys, such as titanium, aluminium, cobalt-chrome-chromium alloys, steels and refractory metals, as well as thermoplastics and ceramics. This process allows to build durable and functional complex parts, no post-curing is required and the build time is fast [162, 171].

Three Dimensional Printing (3DP) concept corresponds to the injection of a liquid binder by a printing head into the surface of a plate, allowing the layer to glue. After the sequential application of layers, the piece is removed and unbound powders are removed. This method can be applied to the production of metal, ceramic, and metal-ceramic composite parts [164].

Direct Ink Writing (DIW), *Ink Jet Printing* (IJP), *Robocasting* [172, 173] or *3D Extrusion Printing* is another type of 3D printing used to develop structures with solid free-form fabrication from an ink with high viscosity. This technique offers great flexibility in the raw materials that can be used and a large range of structure's dimensions and resolutions that can be obtained [174, 175]. The printing occurs with a pressure delivery of an ink through one or multiple capillaries or syringes filament [174, 176, 177].

The main requisite for a successful structure construction with this technique is the development of an ink with suitable rheology [174, 178]. The ink should flow through the nozzle at high shear stresses and then be able to suddenly settle at low stress (i.e., once

out of the nozzle) to achieve shape retention. High viscosity solutions, hydrogels, polyelectrolyte inks, colloidal suspensions, among others, are some materials that can be printed [179] and applied for diverse applications, such as catalytic materials, tissue engineering and composites [180].

This technology presents some advantages that can be important in various areas of research and industrial applications: no restriction on the design/geometry of the printed materials; modification of materials for enhanced performance; materials can be printed from start to finish with no other tooling required; easy to change design and complexity; less waste is created when compared to machining.

Two types of direct ink printing can be used for ink deposition, these are droplet-based writing and continuous filament-based writing [174]. In the first type, the paste is deposited as droplets. The deposit cross sections are discontinuous, as the building blocks are basically overlapping hemispherical droplet splats, and the rheological properties must be within a tighter range.

In the second case, a continuous filament is extruded through a single or multi-nozzle array at a uniform volumetric flow rate. The diameter of the filament depends on the nozzle diameter, paste rheology and printing speed. In this special case, the continuous dispensing allows for a continuous cross sectional area and a wider range of ink rheologies, made to form a shear thinning, particle-filled organic fluid [174].

Figure 2.23 shows an example of a 3D printer with direct ink writing method (a). It is possible to observe the flow through the syringe (b), and then, the printed layers (c).

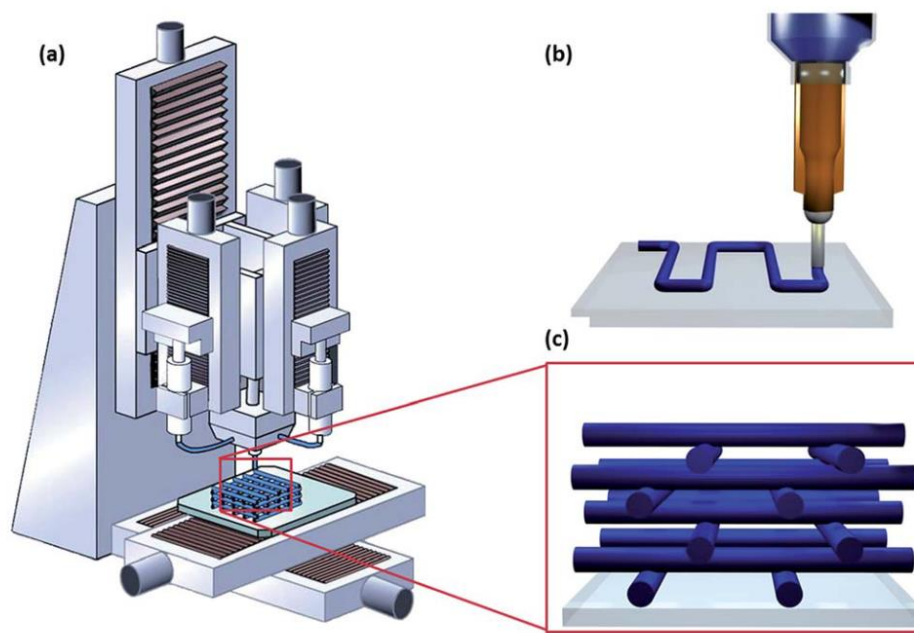


Figure 2.23 - Direct-write layer-by-layer fabrication of a 3D periodic structure: a) image of 3D printer; b) filament deposition; c) microstructure printed using the direct-write technique (from Farahani *et al.* (2014) [181]).

This type of process requires a set of conditions for a successful ink print as explained below. A pump or a syringe connected to a motor mechanism can be used to push inks through an orifice for deposition onto a substrate. To build a 3D geometry, a three-axis motion control system is used to deposit the material according to the defined program [163]. The main factors that influence the printing process are the nozzle design, the motion control system and the pump/motor mechanism.

Nozzle design, including size and shape properties, directly influences the size and shape of the deposited layer, and affects the properties of inks, as for example, viscosity. The use of conical nozzle design enables a large range of viscous materials to be dispensed, combining properties of paste material and factors of printing design.

Motion controller has influence in accuracy and repeatability of the printing, in terms of maximum size of the deposit and the speed at which printing occurs.

Motor mechanism is responsible for flow control, i.e., the speed at which deposition can occur, the accuracy on starting or stopping the printing process, among others. In Gibson *et al.* (2015) [163] is presented the retract/aspirating function available in some types of printers. This configuration allows the retraction of ink during the printing to increase the perfection of the printed piece.

Recently, a few studies about the preparation of 3D-printing adsorbents for CO₂ capture applications have been published (Table 2.11).

Table 2.11. Summary of works about 3D-printed adsorbents for CO₂ capture applications.

Composition of material	P (bar)	T (K)	q (mol·kg ⁻¹)	Ref
ZSM-5 (65%) + bentonite and ludox (35%)	0.10	302	0.80	[182]
SAPO-34 (95%) + graphite (5%)	0.13	303	0.94 0.71	[183]
13X (30%) or 5A (30%) + binders and additives (70%)	0.17	308	0.89 0.89	[184]

Couck *et al.* (2017) [182] reported a monolith produced by additive manufacturing with a mixture composed by 65 wt.% of zeolite ZSM-5 and 35 wt.% of binder (bentonite and ludox). The CO₂ adsorption capacity of the printed material was compared with H-ZSM-5 powder, by measuring the adsorption equilibrium isotherms at four temperatures (283 K, 291 K, 302 K and 309 K) and a pressure range between 0 to 30 bar. They concluded that the presence of binder reduced the adsorption capacity. Recently the same group reported 3D-printed honeycomb-like monoliths of approximately 1 cm in diameter using SAPO-34 zeolite as base material. One of the printed monoliths had 5 wt.% of graphite, however, when compared with powder raw materials, the CO₂ adsorption capacity of the printed materials were much lower than expected [183]. Also, Thakkar *et al.* (2018) [184] presented a 3D-printed composite monolith for CO₂ adsorption from flue gas. Tests with a mixture of zeolite (13X or 5A), binders and other additives were performed. However, CO₂ adsorption capacity measured in the 3D-printed monolith was only 0.89 mol/kg for the materials with 13X and 5A at 0.15 bar and 308 K, because of the low zeolite content of the materials, about 30% by weight.

The incorporation of all parameters cited before, such as, high CO₂ adsorption capacity and high CO₂/N₂ selectivity, good electrical conductivity, high mechanical strength, and a shape feasible to apply in a cyclic adsorption process, is a challenge in this research work.

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3 MATERIALS AND METHODS: DESCRIPTION AND CHARACTERIZATION

In order to develop new adsorbent materials with fixed and appropriate properties, it is important to study some characteristics that can influence the final material.

3.1 MATERIALS SELECTION

Some properties should be taken into account for final monolith production. High selective gas adsorption capacity is one of the most important properties of an adsorbent. However, high strength and stiffness, and also good electrical and thermal conductivities are equally important properties in the produced materials. Raw materials selection could make the difference in the final product. In some cases, in addition to the raw adsorbent materials, additives could be used to improve the specific characteristics of the adsorbent.

3.1.1 RAW MATERIALS

Solid adsorbents such as activated carbons, zeolites and mesoporous silicates, alumina and metal-organic frameworks (MOFs) have been extensively used for gas separation, as pointed out in the state of the art chapter.

It is important to retain that zeolites are inorganic crystalline aluminosilicate structures with high specific surface areas due to the pore channels typically between 2.5 and 10 Å. Their properties, as high stability to temperature variations, high adsorption capacity and low cost, are some reasons for the great use of zeolites in different types of applications. In the internal framework structure of many zeolites, negative charges are balanced with external framework cations, creating a large internal electrical field gradient and an interaction is formed with the molecules that possess a large electric moment. Then, the separation of CO₂ and N₂ from flue gases is benefited [1]. Metal-organic frameworks (MOFs) are another type of material with interconnected pores and they are constructed from metal ions coordinated by rigid organic linkers. There are many studies on MOFs potential for CO₂ adsorption [1-3].

For ESA applications, an electrically conductive material is needed in order for the Joule effect to occur successfully. One component that can be used to incorporate this desired property in the material is a type of activated carbon. Therefore, a review about zeolite adsorbents with high CO₂ capacity and activated carbon was presented in Chapter 2 (state of the art). In addition, a review on the adsorption capacity of some MOFs was also included, as these materials are recently developed adsorbents. However, as zeolites

are more common, present better stability to water and are commercially available, this type of material was selected to be incorporated in the hybrid adsorbent.

Within this class, there are several adsorbents that could be chosen, and the selection was done based on the CO₂ adsorption capacity of each one.

Observing Table 2.6 (section 2.4.2 of Chapter 2), there are three types of synthetic zeolites that stand out for their higher adsorption capacity, especially at low pressures, and are commercially available for use, which are 13X zeolite, 5A zeolite and 4A zeolite.

Another important property of these adsorbents that should be considered due to the presence of water vapour in post combustion streams, 8-15%, is the good stability in the presence of this vapour [4, 5]. Powder of zeolite 13X has a relatively high surface area ($S_{BET} \sim 726 \text{ m}^2 \cdot \text{g}^{-1}$) and high micropore volume ($\sim 0.25 \text{ cm}^3 \cdot \text{g}^{-1}$). Despite the smaller adsorption capacity of the AC, this adsorbent presents excellent electrical properties. Moreover, based on the previous work reported by Ribeiro (2013) [6], an adsorbent with 70% of zeolite 13X and 30% of activated carbon could be a good option for the aim of the work. For these reasons, zeolite 13X and activated carbon were chosen as raw materials.

Table 3.1 presents the list of materials in powder form used in the adsorbent preparation experiments and Figure 3.1 shows the pictures of these powders.

Table 3.1. List of raw adsorbent materials used in the materials preparation.

Designation	Supplier
Zeolite 13X (G5 XP)	CECA Arkema Group
Zeolite 13X (Kostrolith NaMSX P-TR)	Chemiewerk
Activated carbon Maxsorb® MSC-30	Kansai Coke and Chemicals Co, Ltd.
Activated carbon Maxsorb® G08H	Kansai Coke and Chemicals Co, Ltd.

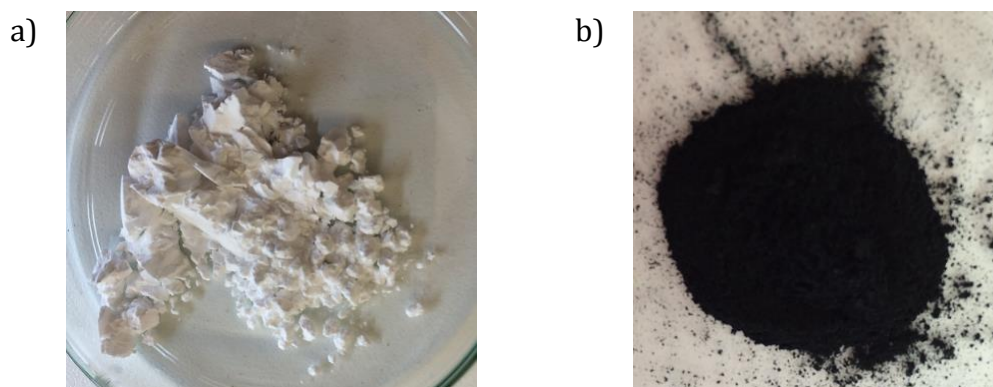


Figure 3.1. Samples used in paste preparation: a) Zeolite 13X; b) Maxsorb activated carbon.

3.1.2 BINDERS AND ADDITIVES

To develop a structured material, additives to bridge the particles together using any mechanism are needed, and these materials can be classified as additives or binders. The function of binders may be designated as agglomerant, plasticizer or lubricant, and the mixture is named as workable when the powders are suitable for moulding, shaping and further processing steps. Depending on the application, one or more types of additives may be used. Binders can be divided into two classes: colloidal or molecular binder; each class is sub-divided into two sub-classes: organic and inorganic. The most common colloidal binders are inorganic clay minerals, as kaolin, ball clay and bentonite. As organic materials, microcrystalline cellulose is the most used material. Molecular binders are used especially to modify the rheological behaviour of the paste, some examples are starch, polyvinyl alcohol (PVA) and methylcellulose (MC). PVA is often used as an adhesion binder and acts by getting adsorbed on the particles. PVA has properties like strength, water solubility, gas permeability and these are heavily dependent on the degree of hydrolysis and on the average molecular weight of the polymer. The residual acetate groups in partially hydrolysed PVA reduce the overall degree of crystallinity, resulting in lower strength and increased water solubility than the fully hydrolysed grades.

In the case of monoliths production with zeolite and activated carbon the literature review demonstrates that methylcellulose, in carboxymethylcellulose (CMC) form, and polyvinyl alcohol (PVA) are the applied binders for activated carbon. Kaolin and bentonite, as well as the CMC and PVA, are the most used in applications with zeolites.

Shams *et al.* (2007) [7] presents the development of granular extrudates of 5A zeolite produced with kaolin and CMC as binders. Grande *et al.* (2006) [8] studied a honeycomb monolith supplied by Coperion Werner & Pfleiderer Stuttgart composed by 4A zeolite and methylcellulose. Lozano-Castelló *et al.* (2002) [9] studied the production of an activated carbon monolith with PVA and an adhesive cellulose. A. Betancur *et al.* (2013) [10] studied the preparation of monoliths from activated carbon using PVA and CMC as agglomerated materials. Balathanigaimani *et al.* (2009) [11] published a work of carbon monolith samples made using three different binders such as polyvinyl alcohol, polyvinyl pyrrolidone (PVP) and carboxymethylcellulose. CMC was used in different quantities, between 5% and 10%. Liu *et al.* (2007) [12] prepared an activated carbon honeycomb monolith by extruding a mixture composed by coal, methylcellulose (2.5 wt.%), bean oil (10 wt.%) and water.

In this application, the main function needed is the agglomeration. Diverse classes of polymers have been developed for binder applications, in order to meet the dual objectives, that are, create a consistent and rigid material with the minimum changes in the raw materials structure, i.e., in zeolite 13X and activated carbon.

In general, works of adsorbent materials production show a study of mechanical characteristics and the adsorption properties, and which is the impact of the use of binders in these properties. It is expected that the binder reduces the adsorption capacity because of the space it occupies and due to crystals blockage. As said before, CMC and PVA are mixed with raw materials in zeolite and activated carbon applications, and in both cases, the adsorption capacity of the original adsorbent is reduced. However, the use of CMC demonstrated better results than PVA, in terms of mechanical properties such as high resistance.

According to this, it was defined that CMC will be included as binders in the methodology of monoliths preparation.

The main properties of this compound are:

- Carboxymethylcellulose is an anionic water soluble polymer produced from naturally cellulose by etherification. CMC can be produced in different chemical and physical properties and it is easily dissolved in water in low quantities. The characteristics of CMC allow establishing and controlling the effects of thickening, binding, stabilizing and water retention of the aqueous systems [13]. The water stability of CMC and the resulting interaction with the water layers supports the agglomerant/plasticizer properties of CMC.

Quantities between 11% and 20% (% by weight) of binder are commonly applied and tested in materials preparation.

Figure 3.2 presents the structure of carboxymethylcellulose and the powder used in experiments. This binder was provided by VWR Chemicals.

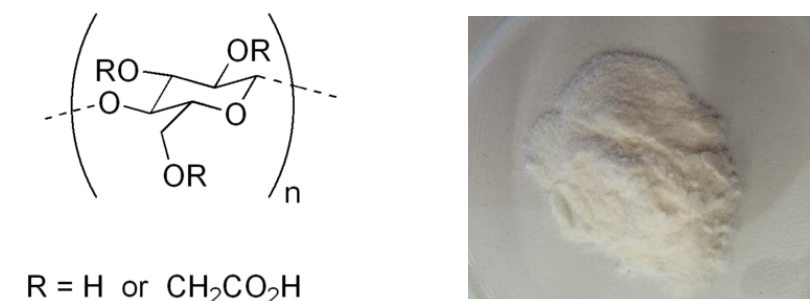


Figure 3.2. Structure of carboxymethylcellulose (left) and image of CMC powder (right).

3.2 MOULDING PROCESS

The production of structures with cylindrical or quadrangular shape without channels or rectangular blocks of different type of composites has been previously attempted [7, 14-18]. A scheme of the process for honeycomb monoliths production was designed, based on the works published in this area, as described in Chapter 2. The process was defined to obtain materials with or without channels.

3.2.1 STEPS

Figure 3.3 illustrates the main steps adopted in the experiments for monoliths production by moulding.

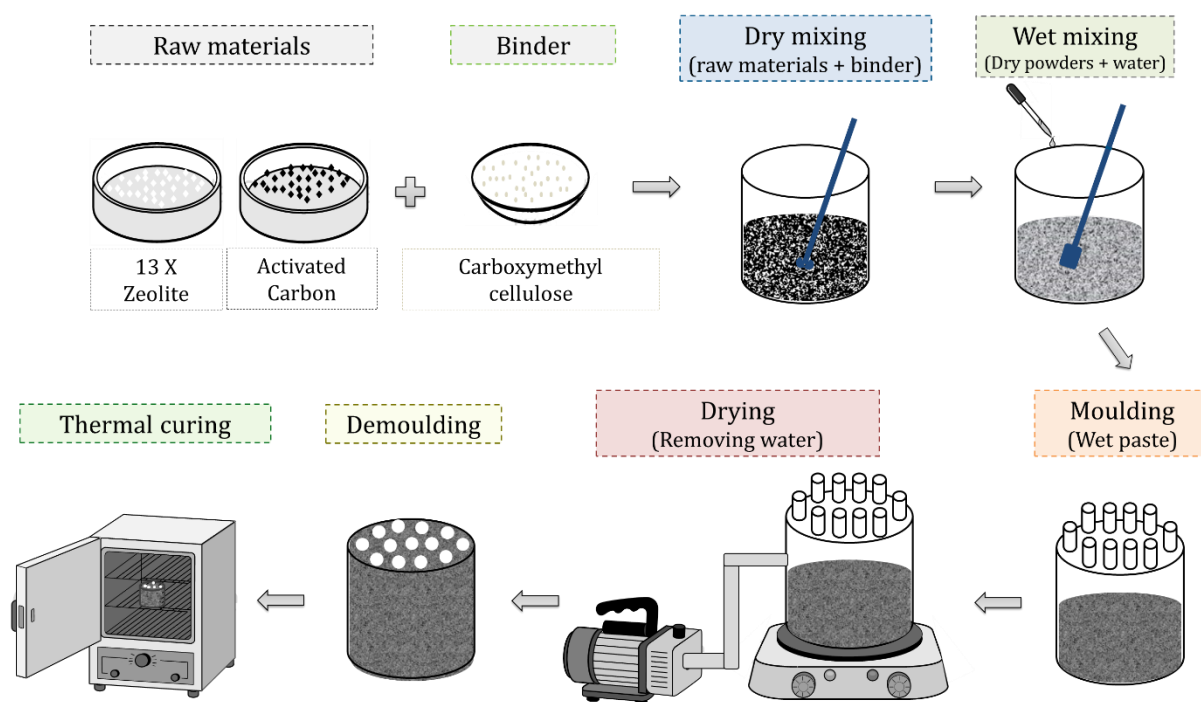


Figure 3.3. Scheme of the methodology used for monoliths production by moulding process.

Initially, the process starts with a mixing step of powder raw materials, binders and additives. Zeolite 13X and activated carbon powders were used as raw materials for honeycomb monoliths production. CMC was added as agglomerating organic binder. After weighing, raw materials and binder, in dry powders form, were mixed with a spatula or a laboratory mixer (Model 712, Fisatom) in order to obtain a homogeneous powder mixture (dry mixing step).

Thereafter, small portions of water were added to prepare a wet mixture, until the paste gets an ideal viscosity for the moulding step (wet mixing step). The paste preparation allowed gaining experience in the estimation of the ideal viscosity, that is, the point at which the paste may be placed in the prepared mould, as well as, in knowing the ideal quantity of water. The paste is formed by mixing with a spatula.

Then, the paste is deposited in a feedhole in order to form a monolith. If a piece with channels is desired, some cylinder sticks with very thin diameter, that could be made of diverse materials, such as, stainless steel, wood or teflon, are introduced in order to create the channels of the honeycomb monolith (moulding step).

In order to remove the excess of water from the slurry, the mould is connected to a vacuum pump. This avoids the creation of air bubbles during the drying and the thermal curing steps. This could be done in two ways: the vacuum pump can be connected to a

recipient where the mould was placed, creating a vacuum ambient; the other way is to connect the vacuum pump directly in the base of the mould while the paste is poured into the mould. In this way, the water is drawn through a filter at the base of the mould. The slurry is added incrementally, providing sufficient time for water drainage. The paste adapts to the mould shape during this step. Also, the mould can be placed in a hot plate to start the first drying (drying step).

After the first drying step, the monolith is removed from the mould (demoulding step). Depending on the mould composition, this process can be difficult. If the drying step has not been sufficient to make a total rigid material, alternatively, the demoulding step can be performed after the thermal curing step (final step of monolith production).

Once the water is removed during the drying step, the formed monolith is submitted to a second heat treatment in an oven at 50°C/60°C for 24 hours. The monolith gains mechanical resistance (thermal curing step).

After the thermal curing process, the monolith should be heated between 60°C and 300°C, in order to remove low molecular weight compounds (water, carbon dioxide, etc.) and this leads to a material weight loss. In this step, while the gases and volatiles are removed, pores and voids are formed. In this work, this post-curing material step is performed in the Rubotherm® balance (experimental set-up described in section 3.6.1) integrated in the activation before the adsorption equilibrium isotherms measurement experiments.

The ratio between raw materials and binders could be varied, depending on the final monolith properties, which could influence for example the strength, the porosity, the pore size distribution.

In this work, the development of hybrid materials started with the moulding process, as presented in this section. During these experiments, some tests were developed and some parameters were optimized, such as, amount of raw materials, solvent and binders. However, the materials produced by moulding were far from the expected results, and it was not possible to continue the studies with this material, that is perform breakthrough experiments and ESA cycles. Nevertheless, being the initial tests, the moulding process and the materials obtained by this method allowed the gain of important knowhow related to the fabrication of new materials and information on the materials performance. In this way, some of the results obtained by this method are presented in Appendix 1.

3.3 EXTRUSION PROCESS

In the extrusion method, the process involved in extrudates/pellets fabrication is slightly different than in the moulding method. In order to produce adsorbent materials, an extruder equipment was used.

3.3.1 CALEVA MULTI LAB EXTRUDER

Caleva Multi Lab Extruder (CLM) is an equipment manufactured by Caleva Process Solutions Ltd, England. This machine includes a function of granulator, extruder and spheronizer (not used in this work) in a single small unit. Figure 3.4 shows the Caleva equipment and Figure 3.5 presents the main components of the extruder required for the materials production, such as, mixing chamber, screw extruder and die.



Figure 3.4. Caleva Multi Lab Extruder.



Figure 3.5. Principal pieces of equipment required for the experiments of materials production.

The CLM-Mixer is intended to be used to prepare wet pastes combining powders with liquid binder(s) rapidly, with the minimum use of material. It is composed of two counter rotating blades within the mixing chamber made of stainless steel. Materials are enclosed during processing to reduce or eliminate the formation of airborne particles. To prepare mixtures with low quantities of powders, a piece of plastic can be used to reduce the mixer volume and keep the material in the processing area.

The CLM-Screw Extruder is intended to be used to process wet granules into dense cylindrical strands of uniform diameter by compressing the material with a screw against a die plate drilled with a series of holes of controlled diameter. The die plate can be replaced to change the diameter of the material produced. This screw rotates horizontally inside the tube. The material to be processed is manually fed from the feed tray and drops down a vertical feed tube onto the screw through a circular opening in the tube. Then, the extrusion screw carries the material forward, compressing it as it approaches the die plate where sufficient pressure will be generated to force the material through the extrusion holes. The feed tray can hold a batch size of up to approximately 40 g.

Two different dies were supplied by Caleva Process Solutions to produce extrudates with 1 or 2 mm of diameter. However, it is possible to fabricate new dies to develop extrudates with other diameters, or materials with different shapes, such as honeycomb monoliths. For this, a new die plate was designed.

Figure 3.6 presents the die plate designed to produce a honeycomb monolith structure. This die was designed considering the restrictions of the extruder equipment, that is size, position and assemble mode of the screw.

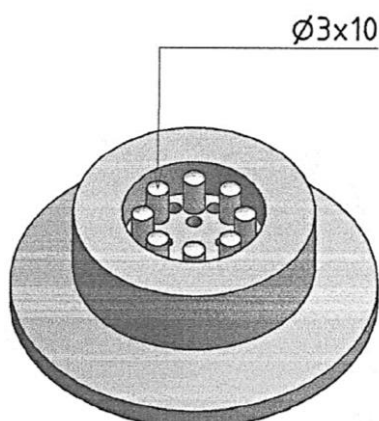


Figure 3.6. Die plate designed to produce honeycomb monoliths.

However, a successful production of honeycomb monoliths with this die was not achieved because two different problems arose. If the paste was very thick, when the material left the holes, it was practically dry, and then the shape obtained was a type of fine cylinders (like “spaghetti”). In the opposite side, if the paste was humid, the material leaving the holes was not dry enough, and the material obtained did not retain the shape. Because of this, the production of a honeycomb monolith structure by extrusion was discarded. Extrudates and pellets were produced with this method.

3.3.2 STEPS

Figure 3.7 illustrates the steps involved in the experiments for pellets production by extrusion process.

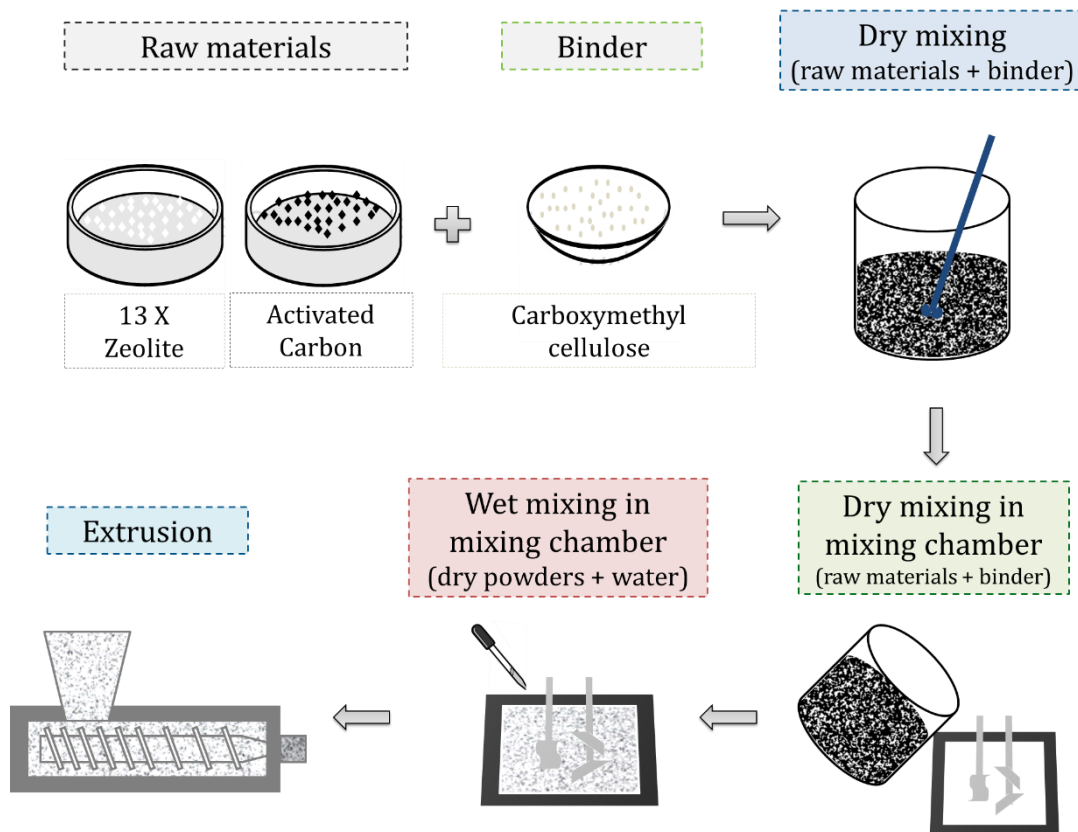


Figure 3.7. Scheme of the methodology used for pellets production by extrusion process.

The dry mixing step is similar to the one described in the moulding process: dry powders raw materials and binders are mixed with a spatula or a laboratory mixer (Mod. 712, Fisatom) in order to obtain a homogeneous powder mixture. At this point, the method is slightly different than the one used in the moulding process. A more efficient

mixture can be achieved in the mixing chamber of the extruder. The powders previously mixed are placed in the mixing chamber before mixing starts. After that, the two opposite rotating blades in the mixing chamber are placed in movement with a specific velocity (dry mixing step).

Once the mixture is homogeneous, it is possible to add water, preferentially, drop by drop, to obtain a good mixture (wet mixing step). With the water addition, the speed of the blades should be reduced. The ideal quantity of water is the most critical point of the experiment. The level of moisture of the wet paste could be analysed through touch. When tightening the wet powders, it is possible to understand if powders stick to one another or if they detach easily. When the quantity of water is sufficient, the blades are stopped.

Then, the wet mixture is removed from the mixing chamber and the paste is inserted in the feed tray. Afterwards, the screw extruder is set in rotation, the paste is manually fed and the extrusion is done through die plate (extrusion step).

3.4 3D-PRINTING PROCESS

3.4.1 ULTIMAKER 2+ AND DISCOV3RY

Ultimaker 2+ 3D-printer (Ultimaker Enterprise, Netherlands) with an extrusion system, Discov3ry (Structur3D Printing, Canada) is the 3D-printing system, commercially available, which was used in this work. Ultimaker 2+ was designed for fused deposition modelling (FDM) technology with an open filament system, optimized by developers for polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), chlorinated polyethylene (CPE), polycarbonate (PC), nylon and thermoplastic polyurethane (TPU 95A). However, it is possible to print with other types of materials prepared for this technology. The equipment has a dimension of 223×223×205 mm. The nozzles available to print have diameters of 0.25, 0.40, 0.60 and 0.80 mm, and depending on the nozzle, layer resolution obtained is between 600 to 20 μm . Another characteristic of the nozzles are the build speed, which is up to 24 $\text{mm}^3\cdot\text{s}^{-1}$, and the printable temperature is between 180 and 260°C, heated in 1 minute. The print head is a swappable nozzle and the travel speed is between 30 and 300 $\text{mm}\cdot\text{s}^{-1}$. The plate is made of glass and can be heated up to 100°C.

Figure 3.8 presents the 3D-printer and Discov3ry. Table 3.2 summarizes the main properties of the Ultimaker 2+.

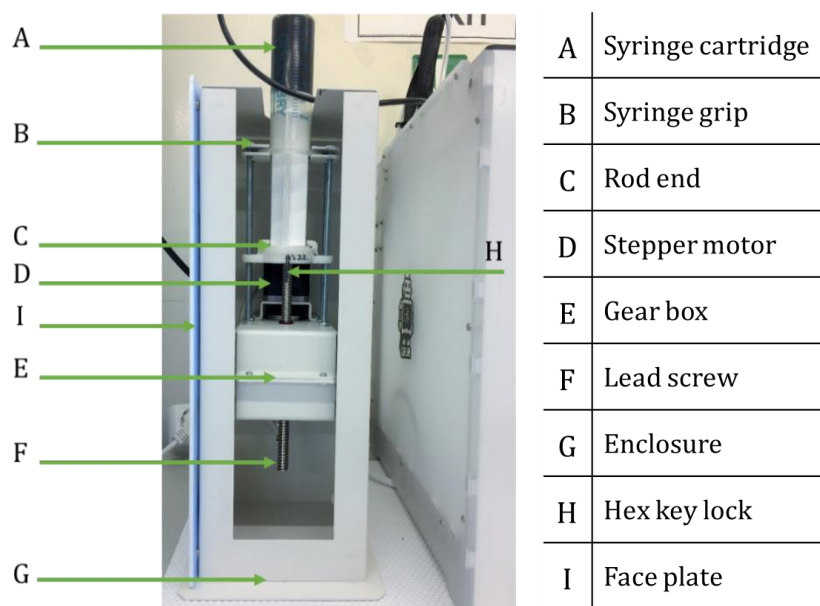
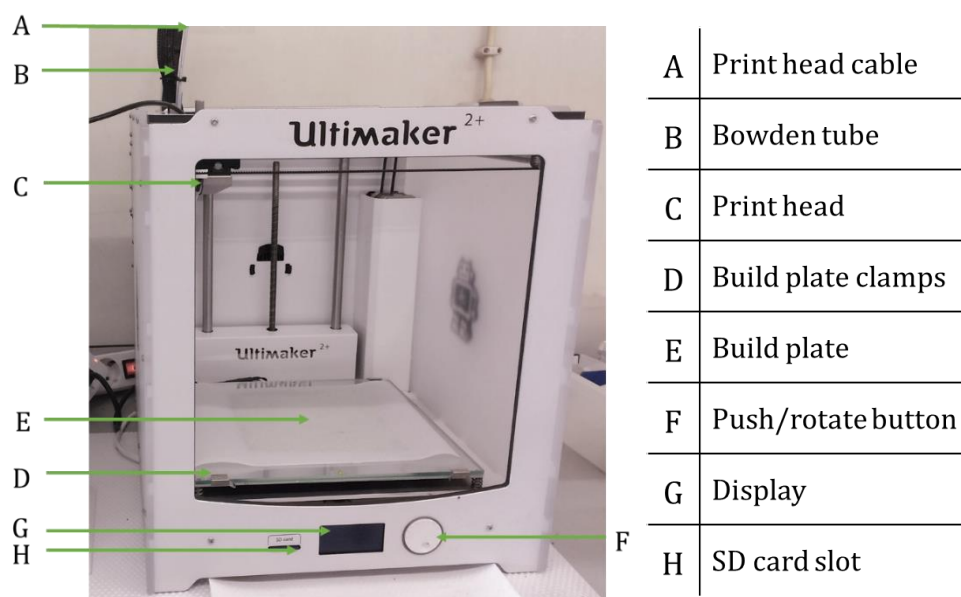


Figure 3.8. Description of equipment for materials production: 3D Printer and Discov3ry.

Table 3.2. Main specifications of Ultimaker 2+ printer.

Specifications	Ultimaker 2+
Dimensions	Machine: 342×493×588 mm Printable space: 223×223×205 mm
Nozzle temperature	180 - 260°C
Nozzle dimension and layer resolution	0.25 mm nozzle: 150 to 600 μm 0.40 mm nozzle: 200 to 20 μm 0.60 mm nozzle: 400 to 20 μm 0.80 mm nozzle: 600 to 20 μm
Build speed	0.25 mm nozzle: 8 mm^3/s 0.40 mm nozzle: 16 mm^3/s 0.60 mm nozzle: 23 mm^3/s 0.80 mm nozzle: 24 mm^3/s
Print head travel speed	30 to 300 mm/s
Build plate temperature	up to 100°C
Type of material printable	PLA, ABS, CPE, PC, PP, PVA, TPU, nylon and others
Software	Ultimaker Cura

This type of extrusion-based 3D printer is composed essentially by two components: the printer and the extruder, which are responsible for the control of movements and nozzle position, and the material flow, respectively. Extrusion system can work by different mechanisms, such as motor driven screw or a pneumatic piston. The stepper motor driven piston system has a motor and a screw that pushes the paste within the syringe, controlling the volume displacement keeping it constant. In this type of operation, the unique disadvantage is the time delay to start and stop the extrusion process, which may result in inaccurate print [19].

Cura® software controls the large number of settings of the 3D-printer.

3.4.2 STEPS

The 3D-printing process used for materials production is very similar when compared with the extrusion process. Types and quantities of raw materials and binders were the same, but the quantity of water had to be tuned.

Figure 3.9 presents the steps involved in 3D-printing process.

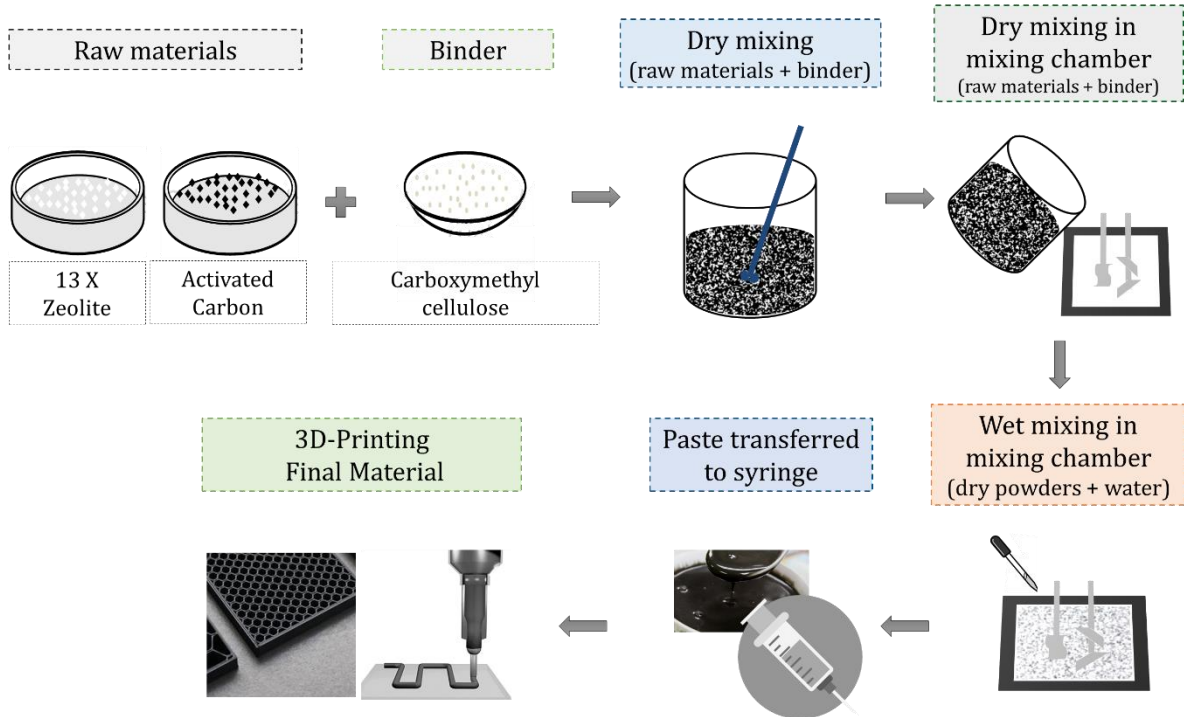


Figure 3.9. Scheme of steps involved in 3D-printing process for materials production.

As can be seen, the steps of wet paste production are similar to the extrusion process. After the preparation of the wet mixture, the ink was transferred to a syringe in order to put in Discov3ry (paste transferred to syringe step). After positioning the syringe, the purge of the system was done and the 3D-printer was prepared to start (3D-printing – Final Material).

3.5 PASTE CHARACTERIZATION WITH RHEOLOGICAL PROPERTIES

The fluids used in 3D-printing can have complex properties. The rheology is the science that studies the behaviour of all kind of materials and how they respond to an applied force. The materials can be defined as fluids or solids. Fluids are characterized by flow properties and the response to deformation defines solids. However, most materials exhibit both behaviours, hence named viscoelastic materials. Viscosity is the main

property used to characterize fluids (Newton Law [20]) and elasticity is used for solids (Hooke's Law [20]). This characterization can be made by a rheometer which can be used to determine the viscosity and the elasticity.

3.5.1 RHEOLOGICAL PARAMETERS – VISCOSITY AND ELASTICITY

Viscosity can be defined as a resistance measurement when a fluid is submitted to a deformation. The equipment used to determine viscosity is a rheometer. In this equipment, the measuring system is chosen according to the samples. The most commonly used systems are constituted by cone-plate or parallel plate configurations. With the experimental tests, some parameters should be estimated, such as, shear stress (τ), force applied in a surface area of the sample, shear rate ($\dot{\gamma}$), speed in a defined thickness of sample and strain (γ), displacement of the sample divided by the thickness. These three properties can be estimated and determined by equations 3.1, 3.2 and 3.3:

$$\tau = \frac{F}{A} \quad 3.1$$

$$\dot{\gamma} = \frac{v}{h} \quad 3.2$$

$$\gamma = \frac{v}{h} \quad 3.3$$

where F is the force applied, A is the area of the plates, v is the speed, h is the distance between plates (gap) and v is the displacement.

After these measurements, viscosity (η) and elasticity or shear modulus (G) can be estimated as the ratio between shear stress and shear rate and between shear stress and strain, respectively (equations 3.4 and 3.5):

$$\eta = \frac{\tau}{\dot{\gamma}} \quad 3.4$$

$$G = \frac{\tau}{\gamma} \quad 3.5$$

During the experiments, when viscosity is estimated, shear stress is controlled and the shear rate is measured, or, vice versa. To estimate the shear modulus, the shear stress is fixed to measure the strain or alternatively a controlled strain allows to determine the shear stress.

Viscosity is determined by shearing a sample and measuring its resistance to that shear. Depending on the behaviour of the viscosity in function of the shear rate, it is possible to define the fluids. This parameter can be dependent or independent of the shear rate, and it is evaluated by flow curves, when shear stress versus shear rate or viscosity versus shear rate are represented. From this analysis, the fluids can be classified as Newtonians (ideal viscous fluids) or non-Newtonians. For Newtonian fluids, viscosity is constant, while for others (non-Newtonians), this is not observed. For these fluids, three types of behaviours can be defined:

- shear thinning or viscoelastic liquid behaviour, denominating the fluids as pseudoplastics, when the viscosity is constant at low shear rates, but decreases, at high shear rates;
- shear thickening or viscoelastic paste behaviour, which corresponds to dilatant fluids, that is, fluids with constant viscosity at low shear rate and increasing viscosity at high shear rate;
- Bingham and Hershel-Bulkley fluids, which are a type of shear thinning fluid, but present a yield stress at zero shear rate.

To characterize Non-Newtonians fluids, the Power-Law generalized fluid model is used. It represents a basic relation between viscosity and strain rate, with the relation presented in equation 3.6:

$$\eta = K\dot{\gamma}^{n-1} \quad 3.6$$

where K is the flow consistency index and n is the flow behaviour index.

This model presents some limitations because it is only valid over a limited range of shear rates. Therefore, K and n are parameters that depend on the range of shear rates considered.

Figure 3.10 presents a summary of all behaviours and establishes a connexion between Power Law parameters and some examples of materials.

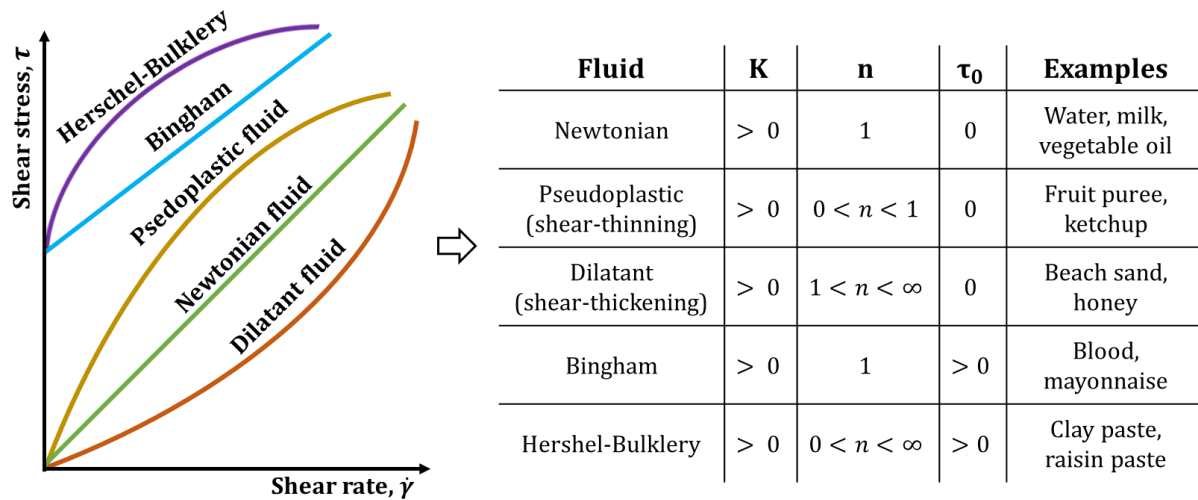


Figure 3.10. Behaviour of different types of fluids (shear stress versus shear rate) and the common parameters for some examples of fluids [21].

The cause of the shear thinning behaviour is justified by the changes in particle/molecular orientations and/or alignment in the direction of flow. When fluids are at rest, the molecules are disordered (high viscosity) and applying a shear rate, a shear thinning is observed and the viscosity decreases as molecules get in order. Some of this type of fluids can present a zero shear viscosity (η_0) in the low shear range, such as amorphous polymers. Zero shear viscosity indicates that a sample's flow curve has a flat plateau at low shear rates where it appears to be Newtonian, and, from this plateau, the η_0 can be extrapolated. There are some models to fit the results of zero shear viscosity fluids, such as, Carreau and Cross models [22].

Generally, pastes, inks or gels at sufficiently high concentrations exhibit three-stage viscous response when sheared over a wide shear rate range. First, Newtonian properties with a constant η_0 are observed at a limited shear range, for low values of shear rates. In the second stage, a range in which the solution viscosity decreases in accordance with the power law relationship is observed, representing the transition between Newtonian to pseudoplastic behaviour. In the third stage, viscosity attains a limiting and constant infinite-shear-viscosity value (η_∞) [23]. These non-Newtonian fluids can be denominated as viscoelastic fluids, displaying both elastic (solid-like) and viscous (liquid-like) properties [24]. As mentioned above, the Cross model can be used to characterize these fluids, which is given by equation 3.7 [22]. This model is a four-parameter model and

describes the general non-Newtonian viscosity versus shear rate curve. It includes a zero shear viscosity, infinite shear viscosity and power law, and shear thinning terms [21].

$$\eta = \frac{\eta_0}{1 + (c \times \dot{\gamma})^p} \quad 3.7$$

where c and p represent the Cross constant and Cross exponent respectively.

Another property that can occur in this shear thinning behaviour is the yield stress fluid, which is the minimum stress required to initiate flow. Fluids with this behaviour exhibit elastic deformation prior to the yield stress and viscous behaviour beyond the yield stress.

Elasticity is a property of viscoelastic fluids which describes the ability of the material to be deformed and its response after deformation. Although fluids with viscous properties dissipate the energy imparted upon them as stress through flow and heat, materials with elasticity have the capacity to remember or store the shape, when stress is applied. These elastic materials, or solid materials in the limit, restore their shape when the stress is removed. Elasticity can be determined by shear modulus. There are two possibilities to evaluate the shear modulus: the rheometer applies a force (shear stress controlled), the sample moves and the strain is measured; or the rheometer applies a fixed deformation to the sample (strain controlled), and the torque needed to achieve a deformation is measured.

In order to determine shear modulus, oscillatory measurements were used which allow to identify how viscous and how elastic is the fluid. Oscillatory tests involve the oscillation of the sample between plates in a sinusoidal manner.

Complex modulus (G^*) is defined as the entire resistance against deformation. In other words, for a perfectly elastic material, the deformation is in phase with the applied shear stress, being the phase angle (δ) equal to 0° , whereas, for a purely viscous material, the deformation is out of phase with applied shear stress (angle of 90°). With the angle phase applied and the complex modulus, storage modulus (G') and loss modulus (G'') can be defined by equations 3.8 and 3.9:

$$G' = G^* \cos(\delta) \quad 3.8$$

$$G'' = G^* \sin(\delta) \quad 3.9$$

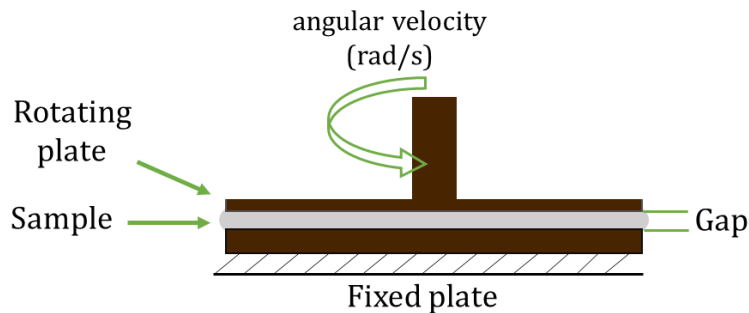
Oscillatory tests estimate the values of storage and loss modulus [25]. The first one, also called as elastic modulus, represents the tendency of material to recoil or retain shape. When the material presents a purely elastic behaviour, it is solid. The second one, also called viscous modulus, represents the tendency of the material to flow. When the material presents a purely viscous behaviour, it is liquid. Between these two behaviours, when G'' is higher than G' , it means that the material is a viscoelastic liquid. When the opposite is verified, G'' is smaller than G' , the material is denominated as viscoelastic solid.

Storage modulus consists of an elastic measure, while loss modulus measures the viscous response. Another important characteristic that can be defined by these tests is the complex viscosity (η^*), which is the ratio of the two moduli and the angular frequency (equation 3.10):

$$\eta^* = \frac{G^*}{\text{angular frequency}} \quad 3.10$$

As explained, viscosity and viscoelastic properties of fluids can be estimated by rotational or oscillation tests.

Figure 3.11 presents the two different measurements [25].



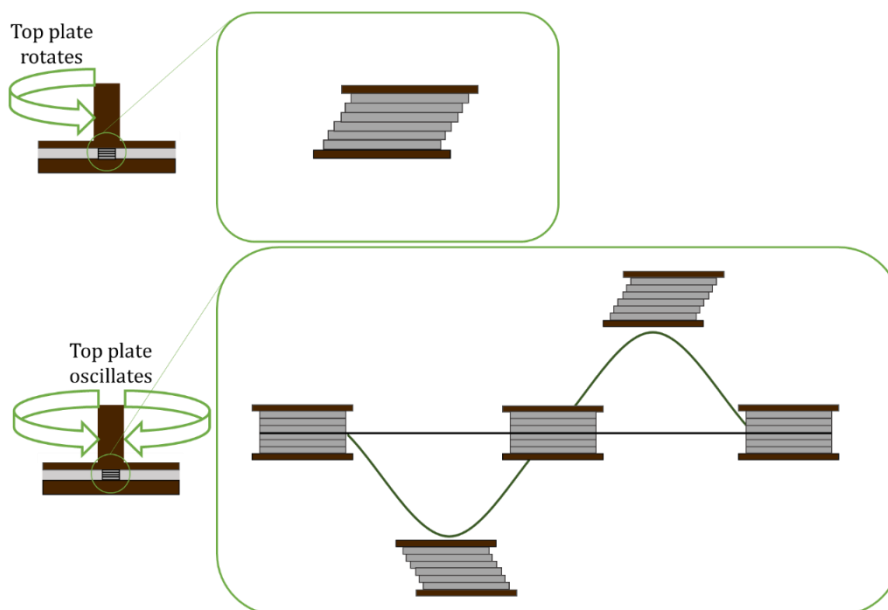


Figure 3.11. Scheme with shear rate applied by rheometer: the first case, the plate rotates continuously; the second case, the plate rotates back and forth (oscillates) (adapted from Nawab *et al.* (2013) [26] and Hill (2013) [27], respectively).

In this work, the measurements were performed in a rheometer (Anton Paar GmbH MCR 92, Austria) using a parallel system plate-plate. To determine the viscosity, analyses were done with a logarithmic ramp profile between 0.001 and 1000 s^{-1} of shear rate. In the oscillatory measurements, the strain was varied with a logarithmic profile between 0.01% and 100% at constant angular frequency of $6.28 \text{ rad}\cdot\text{s}^{-1}$. Both experiments were carried out at 293 K . After the experiments, the data is analysed and the parameters can be calculated.

3.6 CHARACTERIZATION

The characterization of the prepared adsorbents materials is very important. There are several methods to analyse the adsorbent and determine some properties, such as, the morphology and the thermal stability.

3.6.1 HELIUM PYCNOMETRY

Helium pycnometry is a technique used to obtain information about the real density of solids. Due to the small dimension of helium molecules, the smallest voids or pores are filled by helium and the volume of material is calculated, knowing the weight. Combining these results with the bulk or apparent density calculated by other techniques, the

porosity of the material can be obtained. This type of tests was performed at 303 K in a magnetic suspension balance (MSB, Rubotherm®, Bochum, Germany) as was previously applied for other materials in other research works [28-30] (the experimental set-up of He-pycnometry is presented in sub-section 3.7.1).

3.6.2 NITROGEN ADSORPTION AT 77 K

Nitrogen adsorption at 77 K is the most used technique for determination of the surface area of powder or porous materials [31, 32]. The determination of the monolayer capacity combined with the information on the cross-sectional area of the molecule allows the evaluation of the surface area of the solid. This theory is based on a simplified model of physisorption – it assumes that the adsorbent surface has equivalent sites where molecules are adsorbed and that lateral interactions between the adsorbed molecules do not exist. The first adsorbed molecules stay in the first layer and act as sites for molecules in the higher layers.

This technique is applied to determine the mesoporosity and microporosity. Depending on the method used, the mesoporous volume or microporous volume could be determined. Brunauer, Emmett, Teller (BET) model is used extensively to determine the surface area data. This theory is an extension of the Langmuir model and it is valid up to a relative pressure of 0.3 [31].

Nitrogen adsorption isotherms were measured at 77 K with an Accelerated Surface Area and Porosimetry System (Micromeritics' ASAP® 2420, USA). The specific surface area, pore volume and average pore diameter of the samples were determined after activation at 573 K for 12 hours in a vacuum environment before nitrogen adsorption measurements.

3.6.3 CARBON DIOXIDE ADSORPTION AT 273 K

CO₂ adsorption at 273 K is a technique very useful to calculate the narrow micropore distribution in microporous materials since first used in 1964 by Marsh, Walker, and Toda [33]. In contrast to N₂ at 77 K, the higher adsorption temperature of this technique allows easier access to the narrow pores due to the higher kinetic energy of the CO₂ molecules. Then, the surface area of the micropores and their volume, and the micropore size distribution, are obtained by CO₂ at 273 K.

CO₂ adsorption at 273 K experiments were performed with an Accelerated Surface Area and Porosimetry System (Micromeritics' ASAP® 2020, USA), in order to calculate the total pore volume of the adsorbent samples, after activation at 573 K for 12 hours in a vacuum environment. Using the adsorption equilibrium isotherm obtained, micropore size distribution can be calculated by the Dubinin-Radushkevich (DR) equation [34].

3.6.4 MERCURY INTRUSION POROSIMETRY

Mercury intrusion porosimetry is a technique based on the use of a non-wetting liquid and on the non-spontaneous penetration of pores by capillary action. When mercury is placed in contact with a pore opening, the surface tension acts along the line of contact creating a resistance to the entry. The mercury must be forced to intrude the pores of the material by the application of external pressure. This pressure is inversely proportional to the size of the pores; in large macropores only slight pressure is needed, whereas in small pores much greater pressures are required. Then, the progressive intrusion of mercury into a porous structure allows the calculation of volume and size distributions through the Washburn equation (equation 3.11, if pores are cylinder and valid for a pore size range between 0.0018 and 400 µm):

$$D = \frac{-4\sigma\cos\theta}{P} \quad 3.11$$

where σ is the superficial tension, θ is the contact angle and P is the pressure.

This technique allows the calculation of the macroporous and mesoporous distribution, and consequently estimate the porosity from the volume intruded [35]. Mercury intrusion porosimetry is widely used because it is technically easy and also of simple implementation.

Mercury intrusion porosimetry was measured using a Pore Size Analyzer (Micromeritics' AutoPore IV 9500, USA), over a wide range of pressures (0.0007 to 227.5 MPa) after activation at 573 K for 12 hours in a vacuum environment. N₂ at 77 K, CO₂ at 273 K and Hg porosimetry analyses were performed at the University of Malaga.

3.6.5 SCANNING ELECTRON MICROSCOPY

Scanning electron microscope (SEM) was invented 50 years ago and now this technique is applied in many scientific applications [36]. It is a method for high-resolution

imaging of surfaces. In this technique, the sample is hit by a beam of electrons tightly focussed by electromagnetic lenses, generating signals with different types of electrons; backscattered electrons and secondary electrons. These electrons are then collected by an appropriated detector and converted to a signal. To ensure that the electrons efficiently reach the sample and are not absorbed or scattered by the air, the filament is heated in vacuum. The secondary electrons provide information related with the topography of the sample and the backscattered electrons with the sample density.

Different characteristics of the sample can be analysed and measured, such as, the size and form of the crystals or channels, length and wall thickness of the honeycomb monolith [37].

3.6.6 ENERGY DISPERSIVE X-RAY

Energy Dispersive X-Ray Analysis (EDX or EDS) represents one type of chemical microanalysis technique. This system is attached to a Scanning Electron Microscopy (SEM) or a Transmission Electron Microscopy (TEM) to identify the specimen of interest and elemental composition of the material. During the process of electron beam bombardment, an instability on the electrons is created, and some electrons leave the atom shell. Then, electrons from an higher energy orbital move to occupy the vacant lower energy position, resulting in an emission of a specific X-ray energy characteristic each element of the sample, which is detected and measured.

Samples with 1 μm or less can be analysed and the elemental composition characterized by this technique. The main advantages of EDS are high resolution, velocity of analysis and the ease of use to obtain chemical information [38].

Depending on the material analysed, the EDX and microscopy could be insufficient to identify a specimen. In these cases, complementary techniques are available: Fourier Transform Infrared Microscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Surface Analysis with X-ray Photoelectron Spectroscopy (X-ray), and others [39].

The morphology of the samples was studied by Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Spectroscopy (EDS) analysis with High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Backscattered Electron Diffraction Pattern Analysis (FEI Quanta 400FEG ESEM/EDAX Genesis X4M, USA) at the *Centro de Materiais da Universidade do Porto* (CEMUP).

3.6.7 THERMOGRAVIMETRY

Thermogravimetric analysis (TGA) is a method to determine variations of the weight of sample with the increase of temperature in a controlled atmosphere. The equipment can be interfaced with a mass spectrometer in order to identify and measure the gases generated during the temperature increase. The experiments allow the measurement of the thermal stability of materials, the solvent or inert content, the humidity and the percent composition of each component in a sample.

Thermogravimetric analyses (TGA) were performed to evaluate the thermal stability of the adsorbent materials. The experiments were carried out under air, with a heating ramp of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ from 50 to 900°C , using a thermal analyser (STA 409 PC/4/H Luxx Netzsch, Germany).

3.6.8 HEATING TESTS WITH ELECTRIC CURRENT

To study the suitability of the adsorbent materials for Electric Swing Adsorption applications, an electric current was applied in order to observe the Joule effect. Two alligator clips of nickel coated steel were connected to the structure in two points as further apart as possible to conduct the electric current. The cables were also connected to a power supply unit (PSU, Keithley 2440, Newark, USA), that can deliver constant voltage or constant current intensity within 0 to 42 V and 0 to 5 A, respectively. A type K thermocouple was placed in contact with the centre of the sample or the column packed with pellets, in order to measure the temperature history (see Figure 3.12).

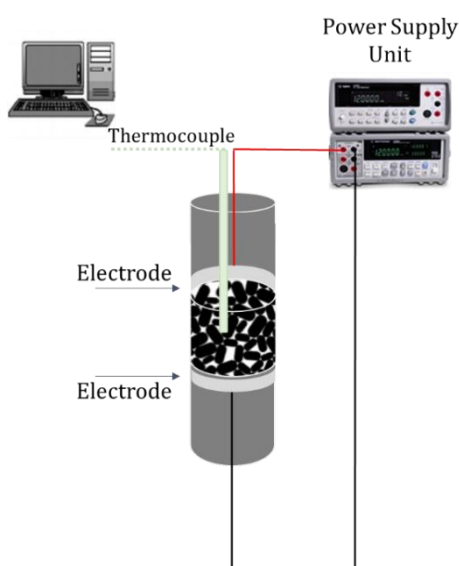


Figure 3.12. Scheme of electrical conductivity tests.

3.6.9 MECHANICAL STRENGTH

Mechanical tests of materials can be divided essentially into two types, which are, methods used to determine the material mechanical properties, independently of the geometry, and methods used to determine the response of a structure to a given action. The second type of referred method measures the crushing strength of a single particle either in axial or in radial direction or both. The first one does not provide the crushing strength of a single entity, but the bulk behaviour and the result is expressed as a weight percentage of fines created during handling in the rotating drum.

Hardness, tensile, impact, fracture toughness and fatigue testing are some examples of the large number of tests that can be done to determine the various mechanical properties of materials.

In this work, the mechanical strength/hardness of the materials produced was studied. A 5Y Tablet hardness tester (Pharmatron/Dr. Schleuniger, Delft), measuring in the range of 1–400 N, was used to perform the tests.

3.7 ADSORPTION EQUILIBRIUM ISOTHERMS

Adsorption is a spontaneous phenomenon characterized by the contact between a fluid (gas or liquid) and the surface of a solid, named adsorbate and adsorbent, respectively. The bonds formed at the surface release heat and the adsorption equilibrium state is achieved [34]. Interactions could be of physical (physisorption) or chemical (chemisorption) type, depending on the type of bonds and energies emitted.

The adsorbate-adsorbent equilibrium can be studied through adsorption equilibrium isotherms measurement, i.e., determining the adsorbed concentration at different pressures or concentrations at a constant temperature [34].

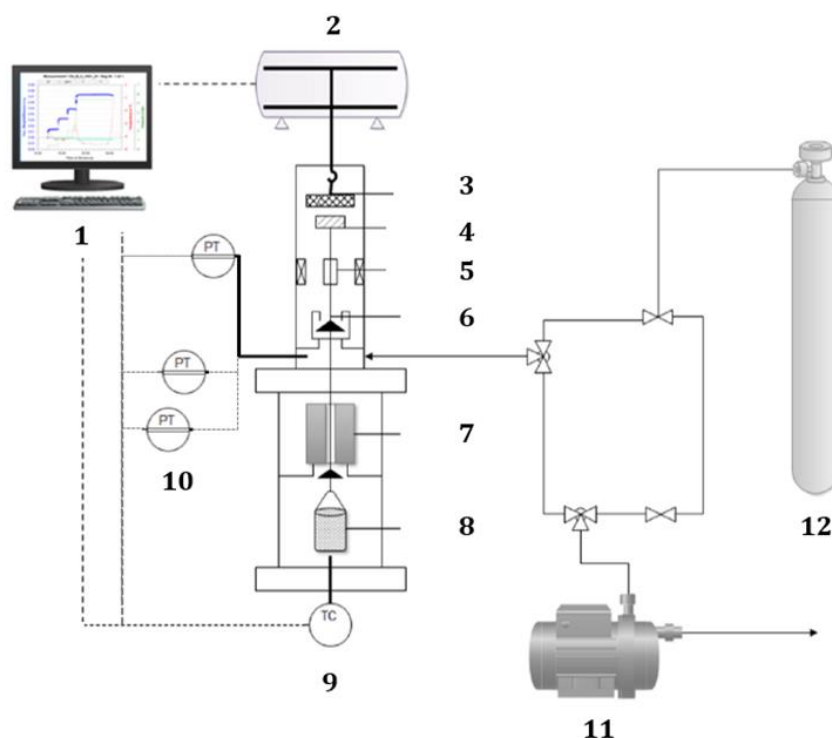
3.7.1 GRAVIMETRIC METHOD - RUBOTHERM®

A gravimetric method using a magnetic suspension balance (MSB, Rubotherm®, Bochum, Germany) with a precision of 0.01 mg was employed in order to measure pure gas adsorption equilibrium isotherms. The system consists of a basket, a permanent magnet, an electromagnet and an analytical balance, as can be seen in Figure 3.13, which represents the diagram of the experimental set-up.

In this equipment, the sample holder is coupled to a suspension magnet, instead of being hung directly to the balance. Using this free suspension coupling, the measuring

force is transmitted without contact from the closed cell where the adsorbent is placed to the Sartorius microbalance, located outside under ambient atmosphere. Inside the balance, the suspension magnet of the MSB has three different vertical positions, corresponding to three different measuring positions.

The Zero point is measured in the first position, where the balance is tared and calibrated. In the second position, the basket containing the sample is lifted up and the mass is weighed. In the third position, a calibrated inert sinker is raised together with the basket and the total mass is weighed. After these measurements, it is possible to obtain the density of the fluid phase in the adsorption chamber.



1 – Computer;	5 – Sensor core;	9 – Thermocouple;
2 – Magnetic suspension balance;	6 – Measuring load decoupling;	10 – Pressures transducers;
3 – Electromagnet;	7 – Sinker;	11 – Vacuum pump;
4 – Permanent magnet;	8 – Basket;	12 – Gas bottle

Figure 3.13. Schematic diagram of the Rubotherm® magnetic suspension balance used in adsorption equilibrium measurements (adapted from Moreira *et al.* (2017) [40]).

As observed in Figure 3.13, the inlet of the balance is connected to a system of valves, which are connected with a gas bottle, for the addition of the adsorbate, and with a

vacuum pump, used for sample activation and cell depressurization. The temperature is continuously monitored by a thermocouple. The pressure inside the cell is measured by three transducers connected to the balance, one operating between 0 and 350 mbar, used to measure data points at low pressures, another one between 0 and 10 bar and finally one that measures from 0 to 100 bar, respectively. The system control and data acquisition are done by a Rubotherm® software. This system can work in a temperature range between 123 K and 673 K, using a cooling jacket or an electrical heater.

The adsorption equilibrium isotherms were measured for CO₂ and N₂ at 303, 323, and 373 K up to 1.5 bar. Before the adsorption measurements, the samples were activated under vacuum at 573 K during 24 hours. When, for each measurement, a stable temperature was observed, pure gas was introduced into the balance. Equilibrium was attained when a constant weight value was obtained. At this point, the measurement of a new point started by adding more gas to the system.

In adsorption equilibrium gravimetric measurements, the weight increase due to adsorption is decreased by the buoyancy effect [41-46]. In this work the buoyancy effects were corrected according to equation 3.12 [47] in order to calculate the correct adsorbed amount in the material:

$$q = \frac{\Delta m + \rho_G (V_s + V_c)}{m_s M_w} \frac{\rho_L}{\rho_L - \rho_G} \quad 3.12$$

where Δm represents the mass difference between the mass given by the microbalance and the initial mass of the basket loaded with the activated sample and the glass wool, V_s and V_c are respectively the volumes of the solid adsorbent and of the permanent magnet plus sample basket plus glass wool used to hold the sample. The density of the gas phase at the measuring conditions (T,P) is denoted by ρ_G , and the density of the adsorbed phase by ρ_L , which is assumed to be equal to the liquid density of the compound at the boiling temperature at 1 atm. The adsorbent mass is given by m_s and the adsorbate molecular weight by M_w . The volume that contributes to the buoyancy effect is V_s , V_c and volume of the adsorbed phase. It is assumed that helium does not adsorb.

3.7.2 MODELS

In 1985, IUPAC defined six types of physisorption isotherms. However, along the years, new types of isotherms have been identified and IUPAC classification of

physisorption isotherms and associated hysteresis loops was updated [48]. The current IUPAC classification is presented in Figure 3.14. Table 3.3 comprises the main characteristics verified in each type of isotherm.

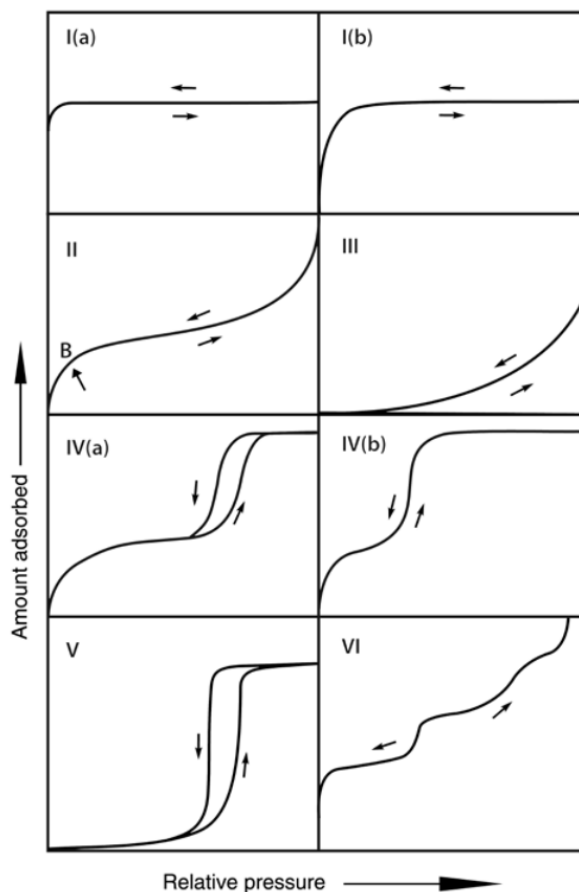


Figure 3.14. Classification of physisorption isotherms by IUPAC [48].

Table 3.3. Type of physisorption isotherms [48, 49].

Type	Phenomena
I	Chemisorption, adsorption in micropores, adsorption in dissolution, physisorption in homogeneous superficies; Usual in zeolites, activated carbons and MOFs.
II	Occurs in monolayer and multilayer coverage, macropores with superficial heterogeneity; Typical of nitrogen adsorption on non-porous or macroporous powders, in carbons or oxides.
III	Weak interactions formed between adsorbate and adsorbent, smaller than the interaction between adsorbate molecules; Adsorption in non-porous and microporous solids and adsorption of water on activated carbons are examples of this type of isotherm.

-
- IV a) Capillary condensation and hysteresis appear in pores > 4nm.
 - IV b) Reversible isotherms (adsorbents with mesopores).
 - V Poor adsorption followed by a capillary condensation.
 - VI Adsorption in homogeneous superfices (each layer is formed when the previous layer is completed).
-

3.7.2.1 LANGMUIR ISOTHERM

In 1918, Langmuir proposed the first theoretically coherent theory of adsorption onto a bare surface, based on a kinetic point of view. The theory predicts that the adsorption is a continuous process in which molecules move, maintaining a zero rate of accumulation at the solid surface, at equilibrium [34]. Three major hypotheses are assumed in this theory: the adsorbent surface is energetically homogeneous, i.e. energy is constant over all sites (ΔH_{ads}), the probability of adsorbing is equal for every active site and each active site adsorbs only one molecule that does not interfere with the neighbour adsorbed molecules. Equation 3.13 presents the Langmuir model:

$$q_i = q_{m,i} \frac{K_i P}{1 + K_i P} \quad 3.13$$

where q_i is the adsorbed amount of the component i, $q_{m,i}$ is the maximum adsorption capacity of the adsorbent (only considering monolayer adsorption) of component i, K_i is the adsorption constant or Langmuir constant of component i, and P is the pressure.

Temperature dependency of the equilibrium constant is expressed by the Van't Hoff equation (equation 3.14):

$$K_i = K_i^0 e^{\left(-\frac{\Delta H}{RT}\right)} \quad 3.14$$

where K_i^0 is the adsorption constant at infinite temperature, $(-\Delta H)$ is the heat of adsorption on the homogeneous surface, R is the universal gas constant and T is the temperature of the system.

3.7.2.2 FREUNDLICH ISOTHERM

This isotherm model was developed by Freundlich as the first empirical and nonlinear equation, considering the adsorption on a non-uniform surface. The model is given by equation 3.15:

$$q_i = K_i P^{\frac{1}{n_i}} \quad 3.15$$

where K_i and n_i are temperature-dependent constants for a particular component, and n_i is calculated by:

$$n_i = A_i + B_i T \quad 3.16$$

where A_i and B_i are parameters relating the thermal variation of the heterogeneity coefficient. K_i is also given by the Van't Hoff equation. When $n_i = 1$, the isotherm is linear. The larger the value of n_i , the more nonlinear the isotherm becomes.

3.7.2.3 LANGMUIR-FREUNDLICH ISOTHERM (SIPS)

The empirical Sips equation, or Langmuir-Freundlich isotherm, results from the combination between Langmuir and Freundlich equations (3.13 and 3.15, respectively). This isotherm is given by equation 3.17

$$q_i = q_{m,i} \frac{(K_i P)^{\frac{1}{n_i}}}{1 + (K_i P)^{\frac{1}{n_i}}} \quad 3.17$$

When $n_i = 1$, the equation is applicable for ideal surfaces, i.e., the Langmuir equation isotherm is obtained.

3.7.2.4 TOTH ISOTHERM

The Toth isotherm was developed to yield an improved fit, when compared with the empirical equations presented before. The Toth equation allows a good description of many systems with sub-monolayer coverage [34] and is given by equation 3.18:

$$q_i = q_{m,i} \frac{K_i P}{[1 + (K_i P)^{n_i}]^{\frac{1}{n_i}}} \quad 3.18$$

3.7.2.5 NITTA ISOTHERM

The Nitta isotherm model [50] is based on statistical thermodynamics and assumes the following: the formation of only one adsorption layer occurs, and the adsorbent surface is heterogeneous, which implies that one molecule adsorbs in more than one active site. The model is represented by equation 3.19:

$$\frac{q_i}{q_{m,i_i}} = a_i K_i P \left[1 - \frac{q_i}{q_{m,i_i}} \right]^{a_i} \quad 3.19$$

where K_i is calculated by the Van't Hoff equation and a_i corresponds to the number of neighboring sites that a molecule can occupy.

Representing the experimental data and the models by these different isotherm equations, it is possible to fit the points and obtain the isotherm parameters for each adsorbate, minimizing the sum of absolute errors between the calculated and experimental values, for example, with the Excel solver add-in.

3.7.3 ISOSTERIC HEATS OF ADSORPTION

Clausius-Clapeyron developed an equation to estimate the isosteric heat of adsorption [34], given by equation 3.20

$$(-\Delta H_i) = RT^2 \left(\frac{\partial \ln P_i}{\partial T} \right)_q \quad 3.20$$

where $(-\Delta H_i)$ is the isosteric heat of adsorption of component i, R is the universal gas constant and T is the temperature of the system. When the difference between heat capacity of the sorbate in adsorbed and vapour phases can be neglected [49], the isosteric heat of adsorption is assumed to be independent of the temperature, and equation 3.20 may be integrated directly obtaining equation 3.21:

$$\ln P_i = \text{constant} - \frac{\Delta H_i}{RT} \quad 3.21$$

Assuming this approximation, plotting P_i versus $1/T$, it is possible to determine the isosteric heat of adsorption through the straight line equation with a slope equal to $-\Delta H_i/R$.

3.8 BREAKTHROUGH CURVES EXPERIMENTS

The rate of adsorption is an important parameter in cyclic adsorption processes. Knowing the diffusion rates of each adsorbate when the adsorption process occurs, i.e., when molecules pass from the bulk phase to adsorption sites, it is possible to design an efficient adsorption separation process. The kinetics of adsorption can be studied by different techniques. In this work, breakthrough curves were performed in a lab-scale fixed bed unit. In addition to the determination of the adsorption kinetics, these fixed bed tests will also be used to validate the measured adsorption equilibrium.

In the lab-scale fixed-bed unit a back-pressure regulator (BPR) (Swagelok, USA) was used to control the pressure inside the system. There are three mass flow controllers (MFC) (Alicat Scientific, USA and Bronkhorst, UK) in the set-up to control the feed gas stream. One flow meter (Alicat Scientific, USA) measured the total flow rate at the column outlet. Labview software is used to control the unit. The composition of the outlet stream of the column is monitored and analysed by an IR detector (LMSxi G4.18, Gas Data Ltd, UK). The total outlet stream of each breakthrough experiment, between 0.150 and 0.350 SLPM, was passed through the IR detector, which is within the permitted range (up to 0.450 SLPM).

Depending on the experiments to perform, different types of columns of stainless-steel material were packed with the appropriate adsorbent.

Figure 3.15 presents a general scheme of set up used in the breakthrough experiments.

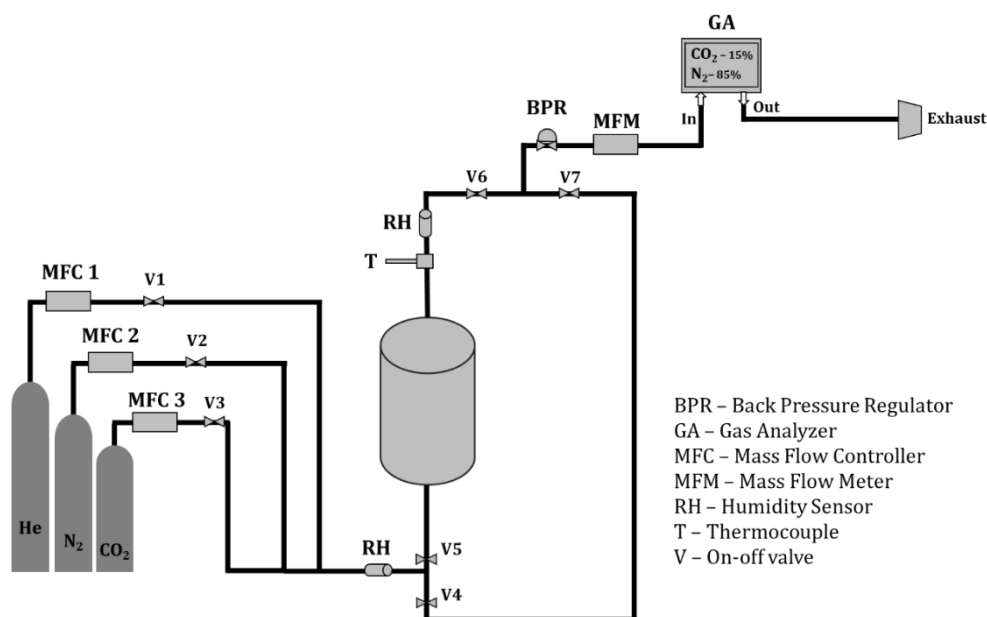


Figure 3.15. Set-up of breakthrough experiments.

3.9 ELECTRIC SWING ADSORPTION CYCLES

The ESA unit equipment is very flexible and allows to perform different types of experiments. The unit is capable of working as a system of Pressure Swing Adsorption, Temperature Swing Adsorption or Electric Swing Adsorption. In all types of processes, it is possible to work with one or two columns, at room or higher temperatures and with condensable compounds, such as, water vapour. All design and a complete description of the unit is presented in the doctoral thesis of Doctor Rui Ribeiro [6].

3.9.1 SUMMARY DESCRIPTION OF THE LAB-SCALE ESA UNIT

The unit is divided into two major parts; one part corresponds to the control/data acquisition deck and the other one to the ESA unit core composed by a gas feed section, a separation section with the adsorption columns, tubing and valves, an analysis system and a power supply/measurement section for the electrification step.

Figure 3.16 illustrates the Electrical Swing Adsorption laboratory unit (a) and the scheme of the respective experimental setup (b).

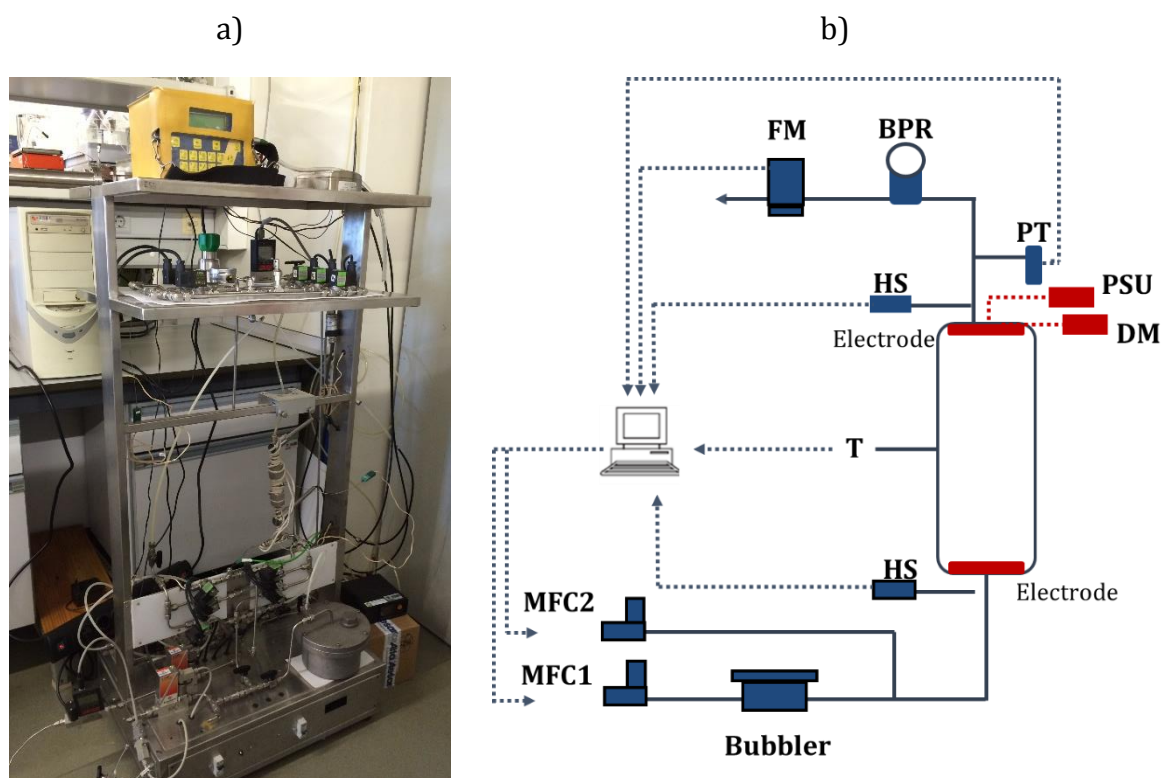


Figure 3.16. a) ESA laboratory unit at LSRE; b) Scheme of the ESA setup (FM – flow meter; BPR – back pressure regulator; HS – humidity sensor; MFC – mass flow controller; PT – pressure transducer; PSU – Power Supply Unit; DM – Digital Multimeter).

The gas feed section has three mass flow controllers (MFC), each one calibrated for one specific component, and a stainless steel bubbler for humidity generation.

The gas separation section is composed of one or two columns and the gas flow is controlled by a system of solenoid, on-off and three way valves. The system is prepared to perform various steps, co-currently or counter-currently. The temperature of the columns can be measured with thermocouples and controlled by a heating rope. The pressure inside the system can be measured with pressure transducers, installed in the column and controlled by two back pressure regulators (BPR).

The analysis section has two different ends for gas exit, one in the top (suitable for recovery of light compounds) and another in the lower part of the unit (for recovery of the heavier gas). Two flow meters installed before the unit exits allow to measure the gaseous flow rate. The composition of the outlet stream of the column is monitored and analyzed by a gas analyzer LMSxi G4.19 from Gas Data Ltd (UK). This instrument detects methane and carbon dioxide by infra-red detectors and oxygen by an electrochemical sensor. If other species are present in the gas stream, a gas chromatograph can be connected.

Figure 3.17 shows the gas data analyzer.



Figure 3.17. Gas data analyzer.

The power supply/measurement section is constituted by a Power Supply Unit (PSU), TSX1820P from Thurlby Thandar Instruments Limited – Tti (UK), and a Digital Multimeter to control and measure the energy supply in the electrification step. The PSU unit can operate at constant voltage or current intensity between 0 and 18 V and between 0 and 20 A, respectively. The voltage or current can be manually controlled with a maximum delivered power of 360 W. The electric current intensity, voltage or electric

resistance are measured in a Programme True RMS Multimeter 1705 from TTi (UK). The multimeter has the capability to measure the voltage and current at the same time. Figure 3.18 presents the power supply unit and digital multimeter.



Figure 3.18. Power supply and measurement section: a) PSU unit; b) digital multimeter.

The signal control and data acquisition deck is divided into two parts: one corresponds to the power supply and the other one to the control and acquisition boards.

The power supply is done by 230 V AC from the public network. Inside the deck, the AC electric current is converted in DC electric current of different voltages to properly supply the different equipment, such as mass flow controllers, flow meters, pressure transducers, back pressure regulators, and solenoid valves with the correct voltage needed. The PID controller power is directly supplied from the 230 V AC network, to control the temperature of the adsorption bed.

Acquisition boards from National Instruments Corporation (USA), for equipment control and acquisition of generated data, are also placed inside the closed deck.

Figure 3.19 presents the National Instruments boards located inside the closed deck.

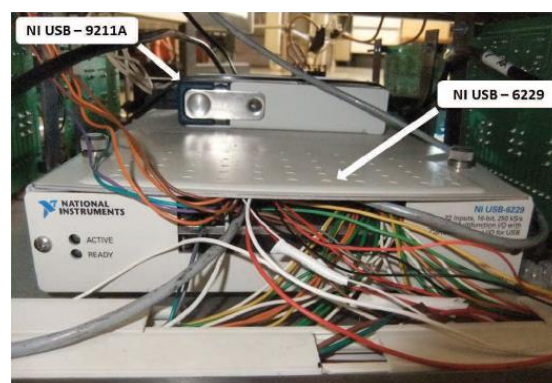


Figure 3.19. National instruments boards.

The control and acquisition of the unit is done with a Labview (Laboratory Virtual Instrument Engineering Workbench) program. Figure 3.20 shows the frontal panel interface of the ESA unit control and acquisition program.

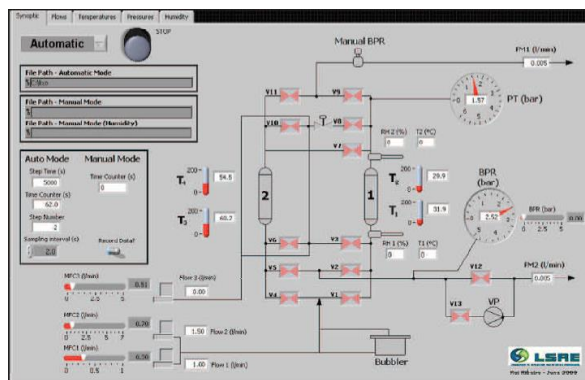


Figure 3.20. Frontal panel interface of the ESA unit control and acquisition program.

NOMENCLATURE AND GLOSSARY

a_i	number of neighboring sites that a molecule can occupy	-
A	area	m^2
A_i	parameter related with the thermal variation of the heterogeneity coefficient	-
B_i	parameter related with the thermal variation of the heterogeneity coefficient	-
c	Cross constant	S
F	force	N
h	distance between plates (gap)	m
G	elasticity or shear modulus	Pa
G^*	complex modulus	-
G'	storage modulus	Pa
G''	loss modulus	Pa
K_i	adsorption constant or Langmuir constant of component i	bar^{-1}
K_i^0	adsorption constant at infinite temperature	bar^{-1}
m_s	mass of adsorbent	kg
M_w	adsorbate molecular weight	$\text{mol}\cdot\text{kg}^{-1}$
n_i	temperature-dependent constants for a particular component	-
p	Cross exponent	-
P	pressure	bar
P_i	partial pressure of component i	bar
q_i	adsorbed amount of component i	$\text{mol}\cdot\text{kg}^{-1}$
$q_{m,i}$	maximum adsorption capacity of the adsorbent of component i	$\text{mol}\cdot\text{kg}^{-1}$
$q_{sat,i}$	adsorbent saturation capacity of component i	$\text{mol}\cdot\text{kg}^{-1}$
R	universal gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	temperature	K
v	displacement	$\text{m}\cdot\text{s}^{-1}$
V_c	the permanent magnet plus sample basket plus glass wool used to hold the sample	m^3
V_s	volume of the solid adsorbent	m^3

GREEK LETTERS

γ	strain	%
$\dot{\gamma}$	shear rate	s ⁻¹
$-\Delta H$	heat of adsorption on the homogeneous surface	J·mol ⁻¹
Δm	is the difference of weight between consecutive measurements	kg
η	viscosity	Pa·s
η_0	zero shear viscosity	Pa·s
η_∞	infinite-shear-viscosity	Pa·s
η^*	complex viscosity	-
ρ_G	density of the gas phase at the measuring conditions (T,P)	kg·m ⁻³
ρ_L	density of the adsorbed phase	kg·m ⁻³
σ	superficial tension	N·m ⁻¹
v	speed	m·s ⁻¹
σ	superficial tension	N·m ⁻¹
τ	shear stress	Pa
τ_0	zero-shear stress	Pa
θ	contact angle	degree

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4 HONEYCOMB MONOLITH BY EXTRUSION PROCESS

Chapter 4 results from the cooperation between LA LSRE-LCM at FEUP and University of Tsinghua in China. The extruded honeycomb monolith material tested in this chapter was supplied by Jingdezhen Jiayi advanced material Co. Ltd., China.

4.1 HONEYCOMB MONOLITH PRODUCTION

In this work, 12 honeycomb monoliths with size of 50×50×50 mm and constituted by 30×30 square channels were produced by Jingdezhen Jiayi advanced material Co. Ltd. The produced material has 70% of zeolite 13X and 30% of activated carbon [1].

Figure 4.1 shows the honeycomb monoliths produced and used in the studies.

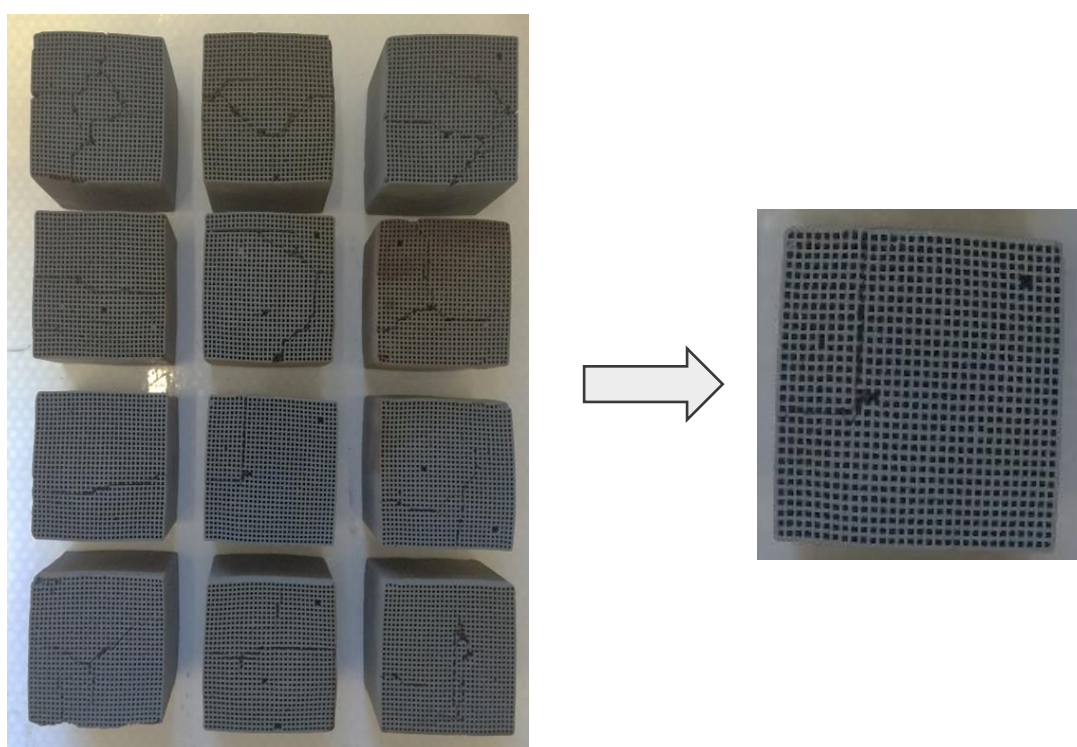


Figure 4.1. Honeycomb monolith with square channels composed of 70% zeolite 13X and 30% activated carbon produced by Jingdezhen Jiayi advanced material Co. Ltd.

The honeycomb monoliths were produced as follows. The solid components employed in the manufacture mixture consist of zeolite 13X (67 wt.%), activated carbon (28 wt.%) and an humic acid (sodium salt) from Acros Organics™ (5 wt.%) as binder material, usually used in the synthesis of organic polymers. The solid powders were mixed in a ball mill to ensure a uniform distribution of all the solid components. After that, water was slowly and drop by drop added to the mixture until a solid weight composition of 80% was obtained. This task was carried out in the ball mill in order to obtain a wet

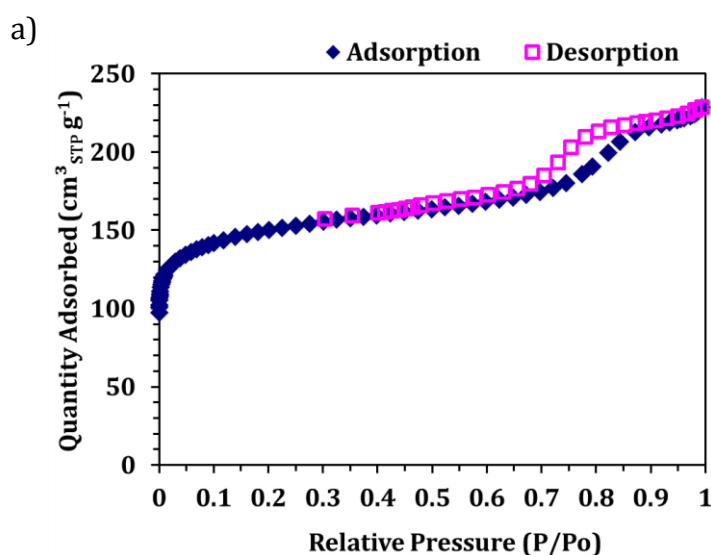
mixture distributed uniformly. Usually, the addition of water to powders can be very difficult due to the viscosity of the paste produced. Therefore, this mixing was carried out for 4 hours. The slurry formed was then pumped to a process of mud pressing and afterwards for a de-airing process where it was purged 5 times by applying vacuum at 0.04 MPa. The honeycomb monolith (shaping of the material) was prepared by an extruding process with 15 tons of force and then dried at room temperature for 24 hours. The final step in the preparation of the green honeycomb monoliths was calcination. This final treatment was performed under vacuum in a furnace at 600°C for 12 hours.

4.2 TEXTURAL CHARACTERIZATION

Textural characterization was carried out based on the specifications presented in Chapter 3. For this material, N₂ adsorption at 77 K, CO₂ adsorption at 273 K, Hg porosimetry, SEM/EDS and thermogravimetric analysis were carried out.

4.2.1 N₂ ADSORPTION AT 77 K

Figure 4.2 a) presents the N₂ adsorption and desorption isotherms at 77 K obtained for the honeycomb monolith after activation at 573 K. Figure 4.2 b) presents the pore size distribution of honeycomb monolith calculated from the adsorption branch of the same nitrogen isotherm at 77 K.



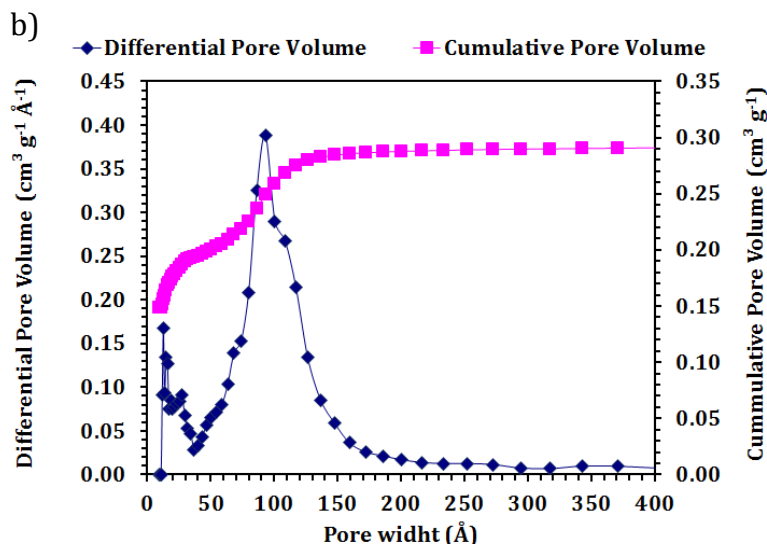


Figure 4.2. Results of a) adsorption equilibrium isotherm of nitrogen on the extruded honeycomb monolith structure at 77 K (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution of the honeycomb monolith calculated from the adsorption branches of nitrogen isotherm at 77 K by the DFT method.

This isotherm shows type IV behaviour as defined by the International Union of Pure and Applied Chemistry (IUPAC), as presented in Figure 4.2 a). Until relative pressures of about 0.1, the adsorbed volume grew rapidly and it is about $140 \text{ cm}^3_{\text{STP}} \cdot \text{g}^{-1}$ at this point, which suggests a large amount of micropores. Above 0.7 of relative pressure another sharp rise of adsorbed volume is observed due to the presence of large mesopores or small macropores. When desorption occurs (open points), hysteresis is verified, suggesting the presence of mesoporosity, and of capillary condensation ([2, 3]). Figure 4.2 b) shows the pore size distribution, determined using Density Functional Theory (DFT), indicating a range of pore widths between 50 and 150 Å.

4.2.2 CO₂ ADSORPTION AT 273 K

In terms of CO₂ adsorption, it is possible to observe its results in Figure 4.3 a), where the CO₂ adsorption equilibrium isotherm at 273 K is presented, and in Figure 4.3 b), where the pore size distribution is presented.

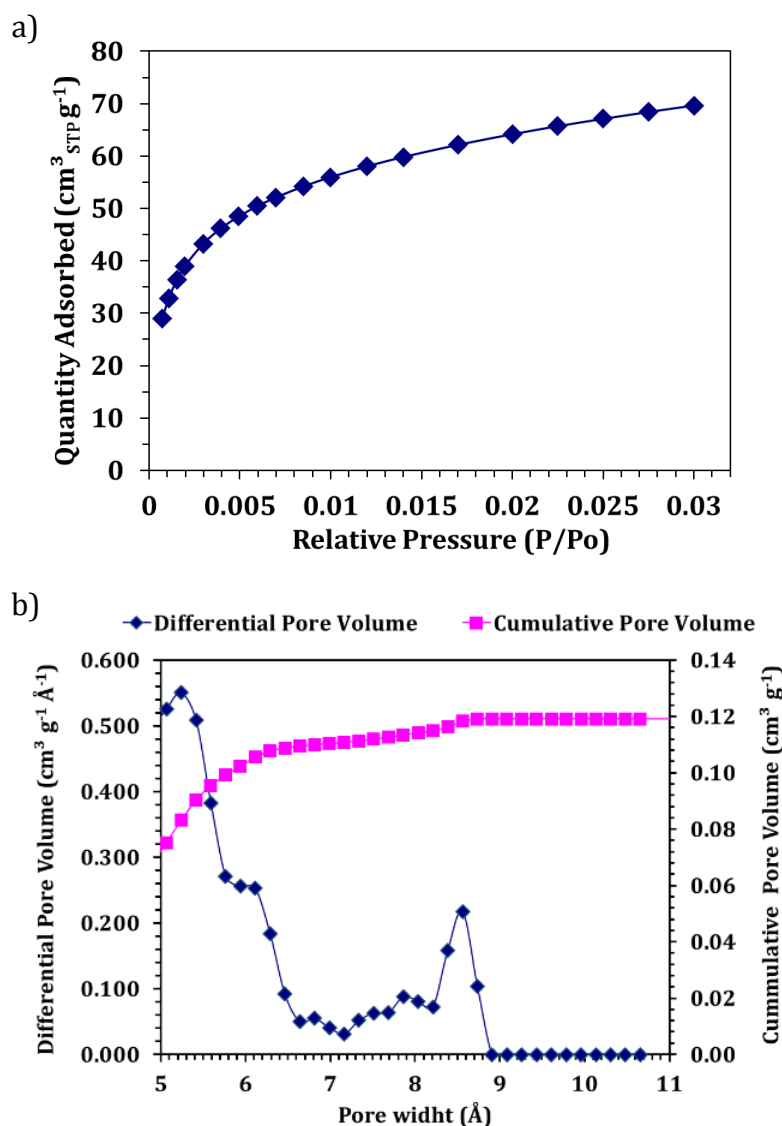


Figure 4.3. Results of a) adsorption equilibrium isotherm of carbon dioxide on the extruded honeycomb monolith structure at 273 K; b) Pore size distribution calculated from the adsorption branches of carbon dioxide isotherm at 273 K by the DFT method.

As can be seen, the isotherm shows a characteristic behaviour of type I isotherm, in general observed in microporous materials. This type of characterization allows access to information on small pores ($< 1 \text{ nm}$) [2].

4.2.3 MERCURY INTRUSION POROSIMETRY

Figure 4.4 presents the results of mercury porosimetry, which indicates an evident range of pore widths between approximately 0.5 to 1 μm . The pores have a narrow distribution, indicative of a uniform pore distribution.

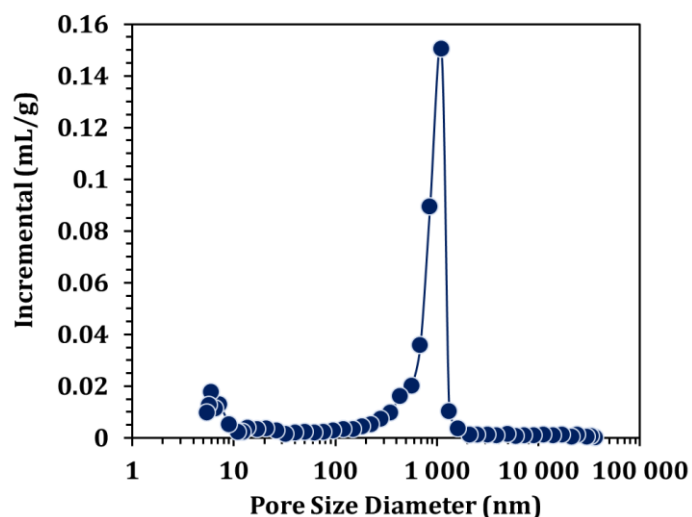


Figure 4.4. Incremental intrusion volume of mercury in the extruded honeycomb monolith sample.

The main results obtained from textural characterization are summarised in Table 4.1.

Table 4.1. Results of textural characterization of the extruded honeycomb monolith.

Parameter	Value
Solid Density ^a (kg·m ⁻³)	1622
Apparent Density ^b (kg·m ⁻³)	796
Monolith wall porosity	0.50

^a determined by helium pycnometry

^b determined from mercury porosimetry at 77 K

4.2.4 THERMOGRAVIMETRIC ANALYSIS

Figure 4.5 shows the TGA curve obtained under air for the extruded honeycomb monolith.

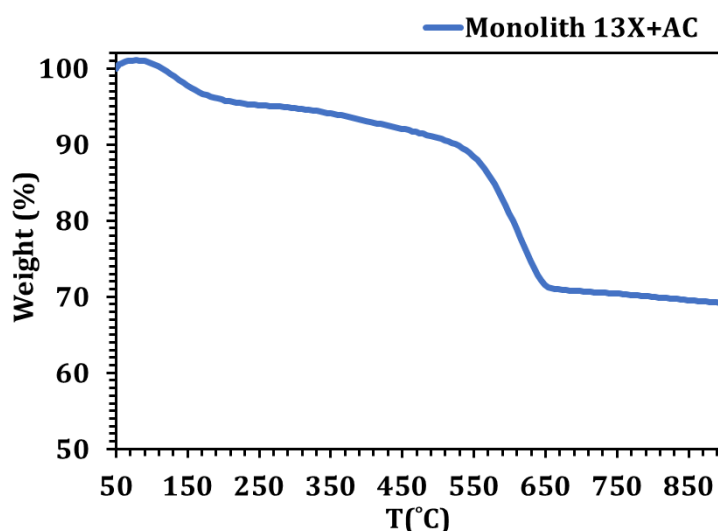


Figure 4.5. TGA curve of the extruded honeycomb monolith decomposition under air.

According to Figure 4.5, up to 900°C, 31.7% of the sample mass is lost. First, until 100°C, the water contained in the sample is evaporated (approximately, 0.5% of the total mass). After that, around 30.5% of volatiles are burned until 630°C, corresponding to the activated carbon and binders used in the monolith preparation. No marked differences were observed on the thermal stability from 630°C to 900°C, and the remaining mass at this temperature corresponds to the zeolite fraction of the monolith. The behaviour observed in this work is in agreement with results reported for other materials containing activated carbon and/or zeolite as raw materials [4-7].

4.2.5 SEM/EDS ANALYSIS

The morphology of the composite material was investigated by SEM micrographs. The results are given in Figure 4.6: a) presents an image of a channel from which it is possible to measure the dimension of a channel (approximately 1 mm) and the wall thickness (about 0.6 mm) (important measurements to be used in the mathematical modelling part); b) shows the topography of the sample; c) and d) show an amplification of the monolith surface and of the interior of the sample, respectively. It is possible to observe a large amount of zeolite crystals and large portions of activated carbon, revealing great heterogeneity; e) and f) show the energy dispersive spectrum of two zones (1 and 2 of c), respectively). Zone 1 (large portion of activated carbon) shows the presence of carbon (C) and oxygen (O), that is, the main elements of activated carbon. In zone 2 (part of zeolite crystal) it is observed the presence of oxygen, sodium (Na), aluminium (Al)

and silicon (Si), characteristic elements of zeolite 13X. The measured Si/Al ratio is about 2. These analyses suggest that the synthesized monolith has high purity.

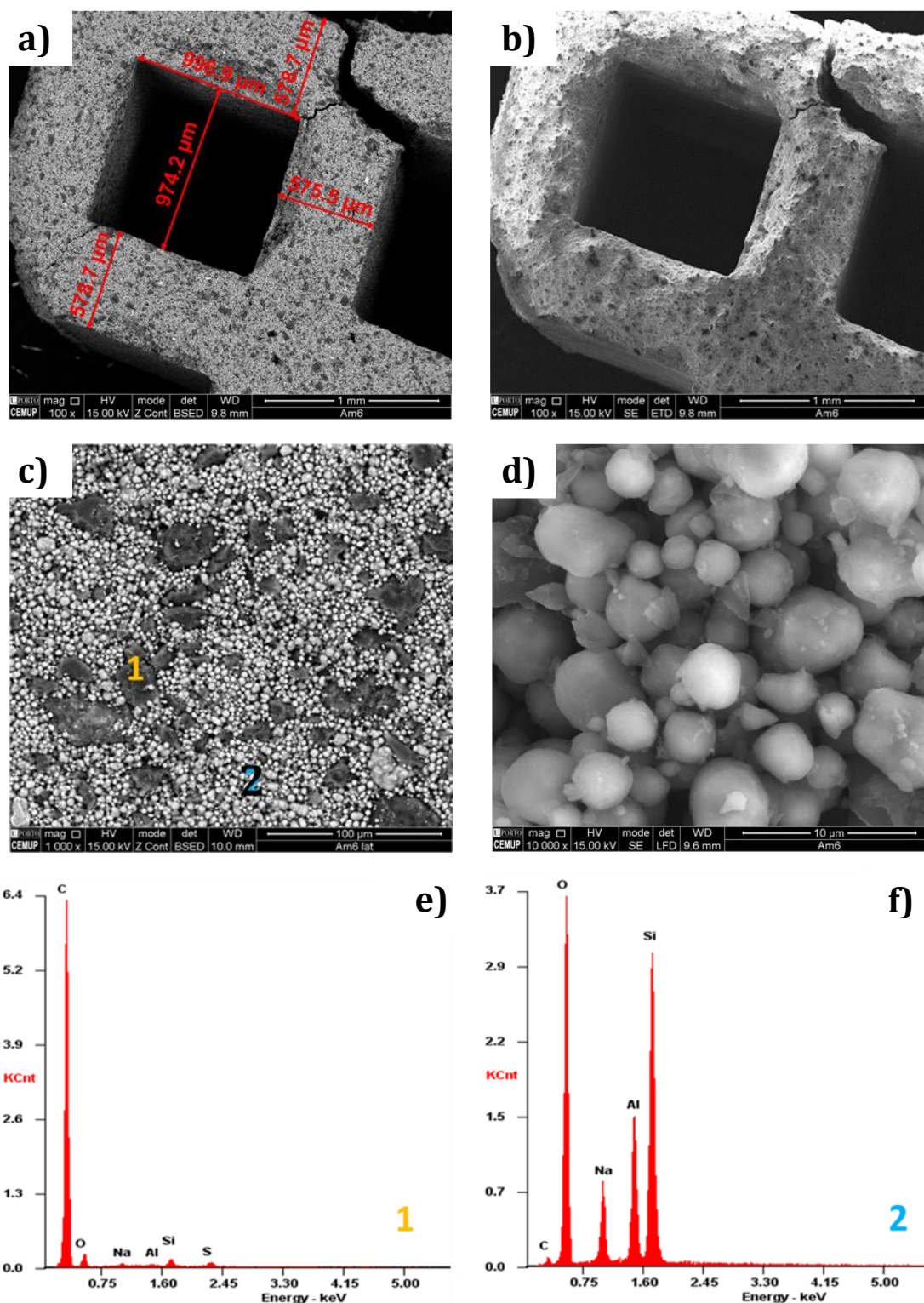


Figure 4.6. SEM photographs of the channel (a), topography of the sample (b), fragment of the extruded honeycomb monolith $\times 1000$ magnification (c), fragment of the extruded honeycomb monolith $\times 10000$ magnification (d), EDS spectra from analysis of zone 1 (e) and EDS spectra from analysis of zone 2 (f).

4.3 MATHEMATICAL MODEL

A mathematical model including mass, energy and momentum balances for multicomponent adsorption in a fixed bed was employed for the simulation of the experimental results. The assumptions considered in the mathematical model ([8, 9]) are:

- Ideal gas behaviour;
- Homogeneous bed porosity;
- No mass, heat or velocity gradients in the radial dimension, only axial dimension is considered;
- Linear Driving Force (LDF) equation for mass transfer in macro and micropores;
- Absence of temperature gradients inside the adsorbent;
- Axial dispersed plug flow.

The gas phase mass balance in a differential volume of the honeycomb monolith is described by equation 4.1:

$$\frac{\partial C_i}{\partial t} + a_m \left(\frac{1 - \varepsilon_m}{\varepsilon_m} \right) k_f (C_i - C_{s,i}) = - \frac{\partial(u_m C_i)}{\partial z} + D_{ax} \frac{\partial}{\partial z} \left(C_t \frac{\partial y_i}{\partial z} \right) \quad 4.1$$

where C_i is the gas concentration of component i , y_i is the molar fraction of component i , $C_{s,i}$ is the concentration at the solid interface of component i , C_t is the total gas concentration, a_m is the honeycomb monolith channel specific area, k_f is the film mass transfer coefficient in the channel wall boundary layer, u_m is the velocity of the gas in each channel of the honeycomb monolith, ε_m is the honeycomb monolith porosity and D_{ax} is the axial dispersion coefficient.

As referred, ε_m is the honeycomb monolith porosity, and it is important to define the method used for its estimation. First, the total volume of the honeycomb monolith was calculated, considering its dimensions of $0.05 \times 0.05 \times 0.05$ m: 1.25×10^{-4} m³. After that, the effective volume occupied by the channels was estimated, considering that the honeycomb monolith has 30×30 channels, and each of them has $10^{-3} \times 10^{-3}$ m. Then, the volume of void space is determined, and a value of 4.5×10^{-5} m³ is obtained. Finally, the porosity is estimated by the ratio between these two volumes. The honeycomb monolith porosity is equal to 0.36.

Another parameter that should be taken into account is the honeycomb monolith channel specific area, a_m , and it can be calculated by the ratio between the specific area and the volume of the solid, as represented in Figure 4.7.

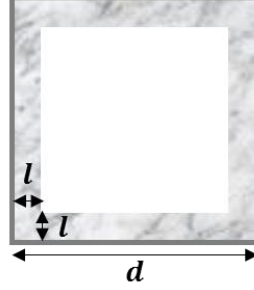


Figure 4.7. Schematic representation of one channel of the monolith.

The value of a_m is given by equation 4.2:

$$a_m = \frac{d - 2l}{l(d - l)} \quad 4.2$$

where the values of d and l are respectively 1.625×10^{-3} m and 3.25×10^{-4} m, as determined by the SEM photography, resulting in a a_m value of 2322 m^{-1} .

Due to the existence of macropores and micropores in the material, two mass balances are written.

The mass balance in the macropores of the honeycomb monolith walls is expressed by a Linear Driving Force model given by equation 4.3:

$$\frac{\partial \bar{C}_i}{\partial t} = k_{macro}(C_{s,i} - \bar{C}_i) - \frac{\rho_w}{\varepsilon_w} \frac{\partial \bar{q}_i}{\partial t} \quad 4.3$$

where k_{macro} is the LDF coefficient, ρ_w is the honeycomb monolith wall density, ε_w is the honeycomb monolith wall porosity, $\bar{C}_i$ is the average concentration at the macropores and $\bar{q}_i$ is the average adsorbed phase concentration.

The mass balance in the micropores is also described using the Linear Driving Force model, expressed by equation 4.4:

$$\frac{\partial \bar{q}_i}{\partial t} = k_{micro}(q_i^* - \bar{q}_i) \quad 4.4$$

where k_{micro} is the LDF coefficient and q_i^* is the adsorbed gas phase concentration of component i in equilibrium with $\bar{C}_i$ (calculated with the Dual-Site Langmuir equation 4.19).

At the honeycomb monolith surface, the fluxes equality can be described by equation 4.5:

$$a_m k_f (C_i - C_{s,i}) = k_{macro} (C_{s,i} - \bar{C}_i) \varepsilon_w \quad 4.5$$

The pressure drop within the adsorption bed is described employing the Ergun equation 4.6:

$$-\frac{\partial P}{\partial z} = \frac{150 \mu_g (1 - \varepsilon_m)^2}{\varepsilon_m^3 4 l_w^2} u_m + \frac{1.75 (1 - \varepsilon_m) \rho_g}{\varepsilon_m^3 2 l_w} |u_m| u_m \quad 4.6$$

where μ_g is the gas viscosity, ρ_g is the gas density and u_m is the interstitial velocity and l_w is the honeycomb monolith wall thickness.

The mathematical model should consider the energy balance for the gas and solid phases and also for the column wall. The gas phase energy balance equation is given by equation 4.7:

$$\begin{aligned} \varepsilon_m C_t \tilde{C}_v \frac{\partial T_g}{\partial t} - \varepsilon_m R_g T_g \frac{\partial C_t}{\partial t} \\ = \frac{\partial}{\partial z} \left(\lambda \frac{\partial T_g}{\partial z} \right) - \varepsilon_m C_t \tilde{C}_p u_m \frac{\partial T_g}{\partial z} - (1 - \varepsilon_m) a_m h_f (T_g - T_s) \end{aligned} \quad 4.7$$

where $\tilde{C}_v$ and $\tilde{C}_p$ are the gas molar specific heat at constant volume and pressure, respectively, λ is the axial heat dispersion coefficient, h_f is the film heat transfer coefficient between the gas phase and the honeycomb monolith channel wall, T_g is the temperature of the gas and T_s is the solid phase temperature.

The energy balance equation to the solid phase is described by equation 4.8:

$$\begin{aligned} (1 - \varepsilon_m) \left[\varepsilon_p \sum_{i=1}^n \bar{C}_i \tilde{C}_{vi} + \rho_w \sum_{i=1}^n \bar{q}_i \tilde{C}_{v,ads,i} + \rho_w \tilde{C}_{p,s} \right] \frac{\partial T_s}{\partial t} = (1 - \varepsilon_m) \left(\varepsilon_w R_g T_s \frac{\partial \bar{C}_i}{\partial t} \right) + \rho_b \left[\sum_{i=1}^n (-\Delta H_i) \frac{\partial \bar{q}_i}{\partial t} \right] + (1 - \varepsilon_m) a_m h_f (T_g - T_s) - \\ \frac{2}{R_c} h_w (T_s - T_w) \end{aligned} \quad 4.8$$

where $\tilde{C}_{v,ads,i}$ is the molar specific heat of component i in the adsorbed phase at constant volume, $\tilde{C}_{p,s}$ is the adsorbent specific heat, ρ_b is the bulk density of the bed, h_w is the film heat transfer coefficient between the honeycomb monolith and the column wall, T_w is the column wall temperature and R_c is the equivalent radius of the monolith (considering approximation to a cylindrical monolith).

Finally, the energy balance neglecting the axial heat conduction of the column wall is described by equation 4.9:

$$\rho_w \tilde{C}_{pw} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_s - T_w) - \alpha_{wl} U (T_w - T_\infty) \quad 4.9$$

where ρ_w is the column wall density, $\tilde{C}_{pw}$ is the column wall specific heat, U is the overall heat transfer coefficient, α_w is the ratio of the internal surface area to the column wall volume and α_{wl} is the ratio of the logarithmic mean surface area of the column shell to the volume of the column wall.

The axial dispersion coefficient (D_{ax}) is calculated employing the Aris-Taylor correlation (equation 4.10):

$$D_{ax} = D_m + \frac{4(R_{ch,e})^2 u_m^2}{192 D_m} \quad 4.10$$

where D_m is the molecular diffusivity of the mixture and $R_{ch,e}$ is the equivalent radius of a honeycomb monolith channel. To determine the $R_{ch,e}$, an approximation to a cylindrical channel was considered. The area of the square channel is set equal to the area of a circumference, and the equivalent radius is estimated.

According to the literature, the Sherwood number in honeycomb monolith structures can be calculated by equation 4.11 [10, 11]:

$$Sh = \frac{2k_f R_{ch,e}}{D_m} = 2.796 \left(1 + 0.190 Re Sc \frac{R_{ch,e}}{L_c} \right)^{0.45} \quad 4.11$$

where L_c is the monolith length, Sc and Re are the Schmidt and Reynolds numbers, respectively, defined by equations 4.12 and 4.13:

$$Sc = \frac{\mu_g}{\rho_g D_m} \quad 4.12$$

$$Re = \frac{\rho_g u_m 2R_{ch,e}}{\mu_g} \quad 4.13$$

The ratio of the internal surface area to the column wall volume (α_w) and the ratio of the logarithmic mean surface area of the column shell to the volume of the column wall (α_{wL}) are determined by equations 4.14 and 4.15:

$$\alpha_w = \frac{4L_c^2}{L_c^3 - \pi \frac{D^2}{2} L_c} \quad 4.14$$

$$\alpha_{wL} = \frac{2}{(D + e) \ln\left(\frac{L_c + 2e}{D}\right)} \quad 4.15$$

where L_c is the monolith length, D is the internal diameter of the column and e is the column wall thickness.

Other heat transfer parameters were calculated using correlations found in the literature ([12]). The required characteristic parameters of the gases were taken from Poling *et al.* (2001) [13].

Heat axial dispersion coefficient is determined by equation 4.16:

$$\frac{\lambda}{k_g} = 7 + 0.5 Pr Re \quad 4.16$$

where Pr is the Prandtl number and k_g is the thermal conductivity of the gas, which can be calculated by equation 4.17:

$$k_{g,i} = \left(\hat{C}_{p,i} + \frac{5 R_g}{4 M_i} \right) \mu_g \quad 4.17$$

where $\hat{C}_{p,i}$ is the weight gas molar specific heat, calculated by the gas molar specific heat at constant pressure and the molar weight of each compound of the mixture.

The film heat transfer coefficient between the gas phase and the monolith channel wall (h_f) is determined by equation 4.18:

$$h_f = \left(2 + 1.1 Re^{0.6} Pr^{1/3} \right) \frac{k_g}{2R_{ch,e}} \quad 4.18$$

Experimental adsorption equilibrium results can be described by many models available in literature, as presented in Chapter 3. One of them is the Dual Site Langmuir equation, and this model assumes that the adsorbent surface is heterogeneous and takes into account two different types of adsorption sites as demonstrated through equation 4.19:

$$q_i = q_{sat,1} \frac{b_{1,i}P}{1 + b_{1,i}P} + q_{sat,2} \frac{b_{2,i}P}{1 + b_{2,i}P} \quad 4.19$$

where q_i is the adsorbed phase concentration, q_{sat} is the saturation capacity, b is the affinity constant and P is the partial pressure.

The temperature dependency of b can be obtained by Van't Hoff ([14]) equation 4.20:

$$b_{k,i} = b_{0,k,i} \exp\left(\frac{-\Delta H_{k,i}}{R_g T}\right) \quad 4.20$$

where $b_{0,k,i}$ is the adsorption constant at infinite temperature and $(-\Delta H_{k,i})$ is the heat of adsorption, for each site k (1 and 2) and each component i , R_g is the universal gas constant, and T is the temperature of the system.

The interaction between the adsorbate molecules and the adsorbent surface is represented by the isosteric heat of adsorption $(-\Delta H)$, which can be calculated from the Clausius-Clapeyron (equation 4.21) [14]:

$$-\Delta H_i = R_g T^2 \left(\frac{\partial \ln P_i}{\partial T} \right)_q \quad 4.21$$

In multicomponent adsorptive processes, it is necessary to understand how the interaction between different species and with the adsorbent surface works. The multicomponent adsorption equilibrium data for CO₂ and N₂ were predicted by the extended Dual Site Langmuir model [15], equation 4.22:

$$q_i = q_{sat,1,i} \frac{b_{1,i}P_i}{1 + \sum_{j=1}^n b_{1,j}P_j} + q_{sat,2,i} \frac{b_{2,i}P_i}{1 + \sum_{j=1}^n b_{2,j}P_j} \quad 4.22$$

where $q_{sat,1,i}$ and $q_{sat,2,i}$ are the adsorption saturation capacities of each site for component i , $b_{1,i;j}$ and $b_{2,i;j}$ are the affinity constants for each adsorption site for component i and j , and P_i is the partial pressure of component i .

The equations presented in this section are solved, coupled with the appropriate boundary and initial conditions, presented in Table 4.2.

Table 4.2. Boundary and initial conditions used in mathematical model simulation.

Boundary conditions	
$z = 0$, inlet	$z = L$, outlet
$u_{m,inlet}y_{inlet}C_{inlet} = u_{m,0}y_{0,i}C_i - D_{ax}C_t \frac{\partial y_i}{\partial z}$	$\frac{\partial C_i}{\partial z} = 0$
$u_{m,inlet}C_{inlet,total} = u_{m,0}C_{i,total}$	$P = P_{outlet}$
$u_{m,inlet}C_pC_{inlet,total}T_{inlet} = u_{m,0}C_pC_{i,total}T_g - \lambda\varepsilon_m \frac{\partial T_g}{\partial z}$	$\frac{\partial T_g}{\partial z} = 0$
Initial conditions	
$y_i = \text{initial composition}$	
$C_{total} = C_{inlet,total}$	
$\frac{dq}{dt} = 0$	
$T_g = T_s = T_w = T_{inlet}$	

The model was implemented in gProms 4.2.0 (PSE Enterprise, United Kingdom) and solved using orthogonal collocation on finite elements method (OCFEM) with second order polynomials over a uniform grid of 150 intervals.

4.4 EXPERIMENTAL CONDITIONS

Breakthrough curve experiments were performed in a lab-scale fixed-bed unit, as described in section 3.8 (Chapter 3).

For these experiments, a stainless steel column with internal cubic ($55 \times 55 \times 55$ mm) shape was designed to pack the adsorbent material. The scheme of the new column is presented in Figure 4.8.

The external structure of the column is a cylinder with 184 mm of length and 120 mm of diameter. The interior is a compartment with a cubic form that supports the honeycomb monolith. Also internally, the top and the base of the column are made in triangular form, as can be seen in Figure 4.8 a), which are filled with glass beads in order to obtain a homogeneous distribution of gas. To prevent the passage of fines into the stainless steel tubes connected to the column, glass wool was placed between each face of the honeycomb monolith and the triangular structures.

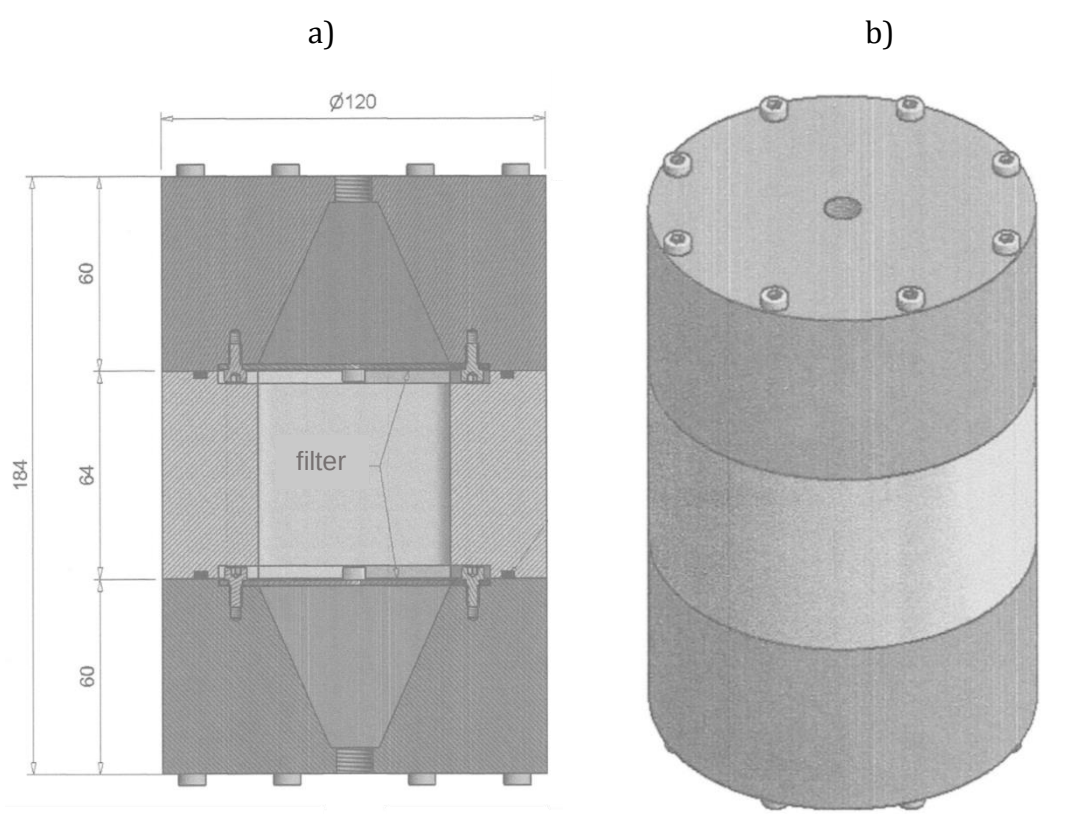


Figure 4.8. Column designed to test the honeycomb monoliths produced by Jingdezhen Jiayi advanced material Co. Ltd: a) internal and b) external view.

The temperature of the gas phase was measured at the column outlet by a thermocouple. The characteristics of the honeycomb monolith adsorbent packed in the column are shown in Table 4.3.

Single and binary breakthrough curves were carried out in accordance with the experimental conditions given in Table 4.4 after the honeycomb monolith activation. This adsorbent with 0.0764 g was activated in situ under 0.200 SLPM helium flow rate at 473 K during 48 hours. After activation, the final mass of adsorbent was 0.0637 g. The experiments were carried out at 298 K.

The experimental data were simulated with gProms using the mathematical model described in sub-section 4.3.

Table 4.3. Characteristics of the honeycomb monolith adsorbent and adsorption bed used for the breakthrough experiments.

Honeycomb monolith adsorbent	
Dehydrated adsorbent mass (kg)	0.0637
Mass loss on activation (wt.%)	20
Bulk density (kg m ⁻³)	510
Porosity	0.36

Table 4.4. Operating conditions employed in the breakthrough curves performed at 298 K with the honeycomb monolith (Ads and Des are abbreviations for adsorption and desorption, respectively).

Run	Initial condition	Flow rate ads/des (SLPM)	Ads feed composition (%)	Des feed composition (%)	Pressure (bar)	Start time desorption (s)
1	He	0.31/0.31	CO ₂ , 21 He, 79	He, 100	2.35	8000
2	N ₂	0.34/0.35	CO ₂ , 19 N ₂ , 81	N ₂ , 100	2.38	10000
3	N ₂	0.33/0.35	CO ₂ , 39 N ₂ , 61	N ₂ , 100	2.38	8000
4	N ₂	0.34/0.35	CO ₂ , 10 N ₂ , 90	N ₂ , 100	2.40	15000

4.5 RESULTS AND DISCUSSION

4.5.1 ADSORPTION EQUILIBRIUM ISOTHERMS

The monolith was characterized in terms of gas adsorption properties with single component adsorption equilibrium isotherms measurements of CO₂ and N₂ at three different temperatures, 303, 333 and 373 K, in the pressure range of 0 to 1.5 bar. Figure 4.9 a) and b) present the measured points, respectively as closed and open for adsorption and desorption. The adsorption equilibrium data obtained experimentally were fitted by

the Dual-Site Langmuir model (equation 4.19). The isotherm parameters for each compound were determined by the minimization of the sum of the absolute errors between experimental and calculated values from pure adsorption equilibrium isotherms and binary breakthrough experiments with the Excel Solver add-in. The parameters obtained are given in Table 4.5.

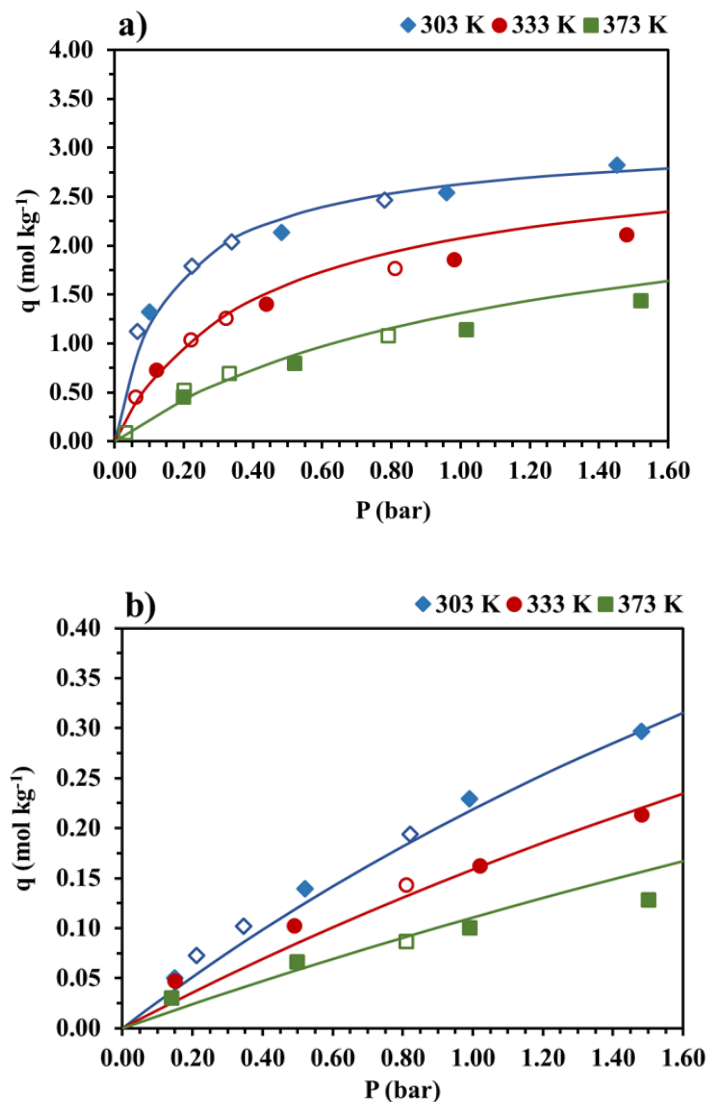


Figure 4.9. Amount of a) CO_2 and b) N_2 adsorbed on the honeycomb extruded monolith: experimental points (closed adsorption, open desorption) at 303 K ($\blacklozenge$), 333 K ($\bullet$), 373 K ($\blacksquare$) and (—) Dual-Site Langmuir isotherm fitting.

Figure 4.9 shows a comparison between calculated adsorption equilibrium isotherms and experimentally obtained data and a reasonably good fit for modelling the adsorption of single component (CO_2 and N_2) is obtained.

In CO₂ adsorption isotherms, it is observed a rapid increase of adsorbed quantity at low pressures (<0.5 bar). Comparing the results with pure powders from literature, at 0.10 bar, the CO₂ adsorption capacities of zeolite 13X is 2.78 mol·kg⁻¹ [16] and of activated carbon is 0.35 mol·kg⁻¹ at 298 K [17], while in this study, the monolith tested presents a capacity around 1.56 mol·kg⁻¹ at 298 K (extrapolating the Dual Site Langmuir fitting for this temperature). The reduction in adsorption capacity when compared with the expected value (considering 70% zeolite/30% activated carbon) is about 24% (0.49 mol·kg⁻¹), showing some disadvantages of the binding agents added in the honeycomb monolith preparation. Besides that, the extrusion process could have also slightly reduced the adsorption capacity [18]. Despite the fact that this capacity is lower than expected, these values indicate that this composite material is promising to apply in cyclic adsorption processes, due to the honeycomb monolith structure and good selectivity for CO₂. Comparing the adsorption capacity of this honeycomb material with another honeycomb monolith composed by zeolite and carbon reported by Masala *et al.* (2017) [19], CO₂ and N₂ adsorption capacity of material with 78% H-ZSM-5/22% carbon is 1.00 mol·kg⁻¹ and 0.062 mol·kg⁻¹, respectively, at 0.10 bar and 298 K (which compares with 1.56 mol·kg⁻¹ and 0.028 mol·kg⁻¹ for the material reported in this work). However, particularly for ESA applications, the electric resistivity or conductivity of material is an important characteristic that should be taken into account due to the Joule effect implementation. At room temperature, the resistivity of zeolite 13X/activated carbon honeycomb monolith is around $3 \times 10^5 \Omega \cdot m$, which indicates that the material has poor electrical conductivity characteristics when compared, for example, with a H-ZSM-5/carbon material with a reported value of resistivity of 5.8 $\Omega \cdot m$ [19]. This property is a limitation of the material for application in ESA process. Modifications in the material preparation should be considered in order to increase the number of charge carriers, and consequently, improve the conductivity.

As mentioned above, the information on the adsorption capacity obtained with the binary breakthrough curves was included in the determination of the fitting parameters of the Dual-Site isotherm. Figure 4.10 shows the experimental results obtained for the multicomponent adsorption equilibrium and respective fitting.

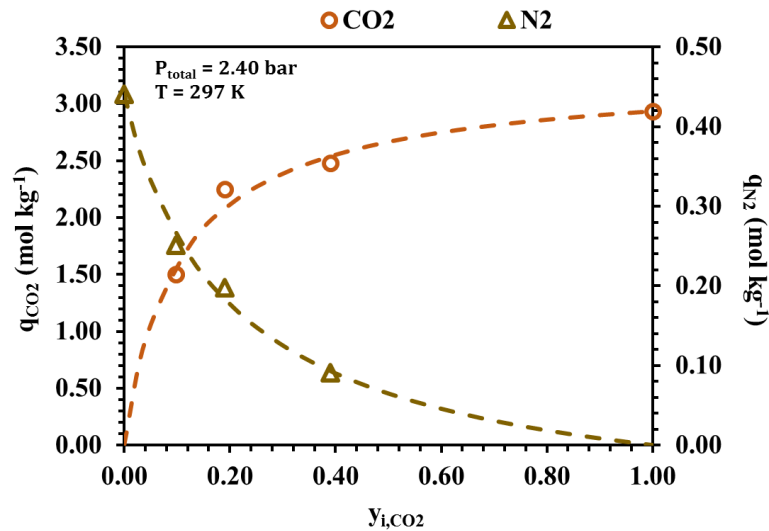


Figure 4.10. Binary experimental results of adsorbed amounts of carbon dioxide and nitrogen for three different composition feeds. Points represent the experimental adsorption results and dashed lines represent the Dual-Site isotherm fitting.

Table 4.5. Fitting parameters of the Dual-Site Langmuir model for CO₂ and N₂ single component adsorption equilibrium on the extruded honeycomb monolith.

Species	$q_{\text{sat},1}$ (mol·kg ⁻¹)	$q_{\text{sat},2}$ (mol·kg ⁻¹)	$b_{0,1}$ (bar ⁻¹)	$b_{0,2}$ (bar ⁻¹)	$(-\Delta H)_1$ (kJ·mol ⁻¹)	$(-\Delta H)_2$ (kJ·mol ⁻¹)
CO ₂	2.432	0.696	1.35×10^{-4}	3.00×10^{-6}	27.6	34.0
N ₂	0.179	1.044	2.09×10^{-2}	1.95×10^{-3}	7.1	11.6

The equilibrium selectivity (α_{12}) of an adsorbent can be calculated as follows:

$$\alpha_{12} = (Y_1/X_1)/(Y_2/X_2) \quad 4.23$$

where Y and X are respectively the adsorbed and gas phase molar fractions of components 1 and 2 [20]. Calculating this value for the multicomponent adsorption of CO₂ and N₂ of Run 4 a value of 54.0 is obtained. It should be noted that this value represents the multicomponent competitive equilibrium selectivity.

4.5.2 ISOSTERIC HEATS OF ADSORPTION

From the equilibrium results, the experimental isosteric heat of adsorption can be determined as a function of the amount adsorbed. For this purpose, the Clausius-

Clapeyron (equation 4.21) is employed. The values calculated are presented in Figure 4.11.

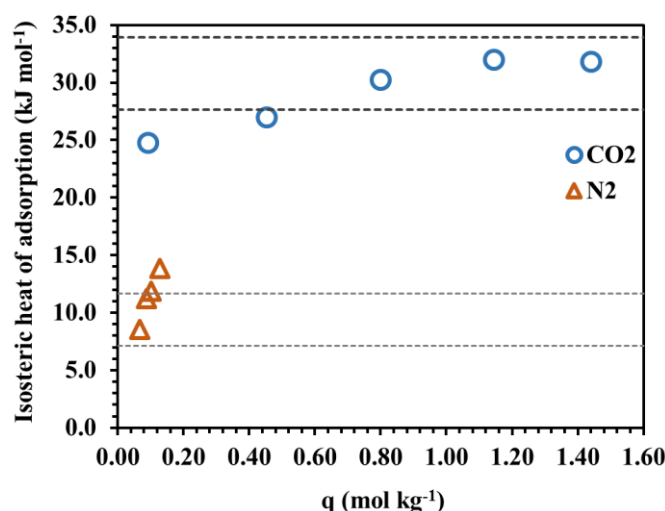


Figure 4.11. Single-component isosteric heats of adsorption obtained for CO₂ (●) and N₂ (▲) as a function of the amount adsorbed in the temperature range of 303 to 373 K. Dashed lines represent the values obtained by the fitting of Dual-Site Langmuir model.

Observing Figure 4.11, an increase of the values of the isosteric heats of adsorption with the loading is observed, which may indicate the presence of attractive lateral interactions between the adsorbed molecules [21]. The values of the isosteric heats of adsorption vary between 25 and 32 kJ·mol⁻¹ for carbon dioxide and between 9 and 14 kJ·mol⁻¹ for nitrogen. These values are within the range of values reported in the literature for both materials of the composite honeycomb monolith. Namely, in the case of carbon dioxide, for zeolite 13X values of 34 kJ·mol⁻¹ [22] and 37 kJ·mol⁻¹ [16] have been reported. For activated carbons, the range of reported values is wider due to the diversity of materials and can vary between 23 to 29 kJ·mol⁻¹ [23-25]. A similar trend is observed for nitrogen, as values between 13 and 17 kJ·mol⁻¹ [16, 22] have been reported for zeolite 13X and values between 11 and 17 kJ·mol⁻¹ for activated carbon [23-25]. Taking into consideration the honeycomb monolith composition, that is, the weight percentage of carbon and zeolite, the values obtained for the monolith can be estimated as approximately the weighted average reported in the literature for the two types of adsorbents. This behaviour, e.g. values of isosteric heat of adsorption for carbon/zeolite composites lower than values for CO₂ in zeolite 13X, have been reported previously in the

literature [26, 27]. Furthermore, the experimental values of the isosteric heat of adsorption are in accordance with the values obtained by the Dual-Site model.

4.5.3 BREAKTHROUGH EXPERIMENTS

Breakthrough curves were measured in accordance with the experimental conditions reported in Table 4.4 (4.4 Experimental conditions) and the results are reported in this section. In addition to the fixed-bed experimental data, the simulation results of the developed mathematical model are compared with the experimental results.

At the beginning of each experiment, the column is filled with He or N₂ at the feed temperature and pressure. In the adsorption step, the gas mixture is fed to the column until saturation. Afterwards, the desorption step is carried out with a change in the inlet stream to helium or nitrogen, depending on the experiment. In the adsorption and desorption steps, the total volumetric flow rate was kept constant. The volumetric flow rate, the molar fraction and temperature history at the column outlet was recorded.

The values of the transport parameters were determined at the conditions of the respective feed mixture of each breakthrough curve by commonly used correlations as described in section 4.3 Mathematical Model.

Values of α_w and α_{wl} were calculated to be 22 and 32, respectively. Table 4.6 presents the values of the transport parameters used in the simulations.

Table 4.6. Transport parameters values used in the simulation of the breakthrough experiments.

Run	k_{macro} (s ⁻¹)	k_{micro} (s ⁻¹)	D_{ax} (m ² ·s ⁻¹)	k_f (m·s ⁻¹)	h_f (W·m ⁻² ·K ⁻¹)	h_w (W·m ⁻² ·K ⁻¹)	U (W·m ⁻² ·K ⁻¹)
1	47	11	2.5×10^{-5}	1.2×10^{-3}	3.8	26.1	17.3
2	14	0.003	6.4×10^{-6}	3.2×10^{-4}	0.48	2.5	2.4
3	17	0.003	6.3×10^{-6}	3.1×10^{-4}	0.58	3.2	3.0
4	14	0.003	6.3×10^{-6}	3.1×10^{-4}	0.42	2.2	2.1

These values were calculated for each experiment. They were kept constant during the simulations and no fitting was done, except for the linear driving force coefficients (k_{macro} and k_{micro}) that were fitted. Note the difference between the values of the parameters for run 1 when compared with run 2, 3 and 4. These differences are due to the

feed mixture composition, that in the first experience is composed by carbon dioxide and helium while for the others is carbon dioxide and nitrogen. Effective diffusional time constants of 0.007 s^{-1} at 293 K [28] and 0.003 s^{-1} at 298 K [27] have been reported for CO_2 in zeolite 13X powders. These values are in accordance with the values of k_{micro} reported in Table 4.6.

To check the viability of carbon dioxide and nitrogen separation by adsorption, fixed bed adsorption experiments with single feed (Run 1) and binary mixtures (Run 2, 3 and 4) were carried out. Figure 4.12 to Figure 4.15 present the obtained CO_2 molar flow rate (a), the CO_2 molar fraction (b) and the total flow rate (c) at the column outlet for each run (1, 2, 3 and 4 respectively).

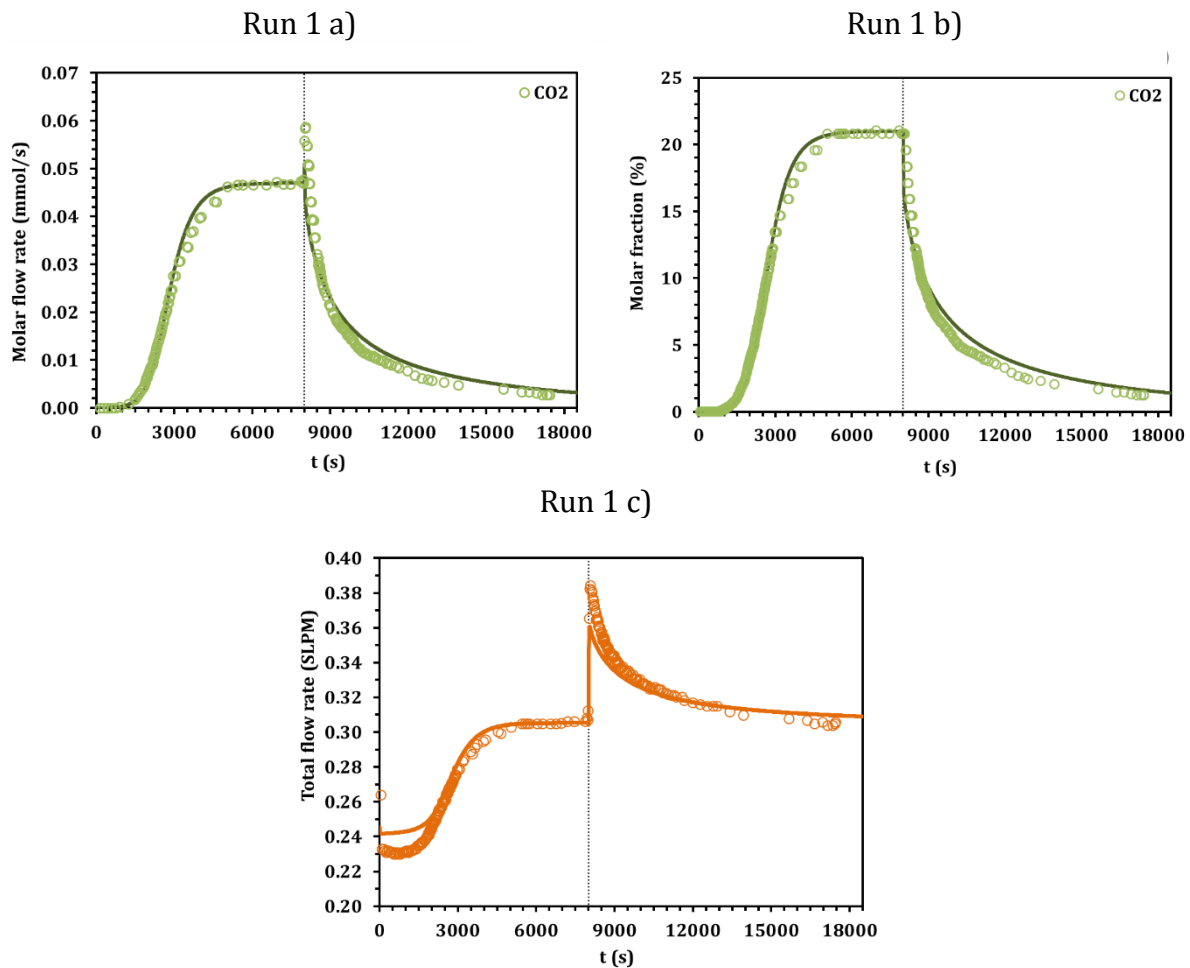


Figure 4.12. Breakthrough curve results of run 1 for inlet total pressure of 2.35 bar at 298 K: CO_2 molar flow rate at the column outlet (a), CO_2 molar fraction at the column outlet (b) and total flow rate at the column outlet (c). Points - experimental data; lines - model. Vertical line - beginning of desorption.

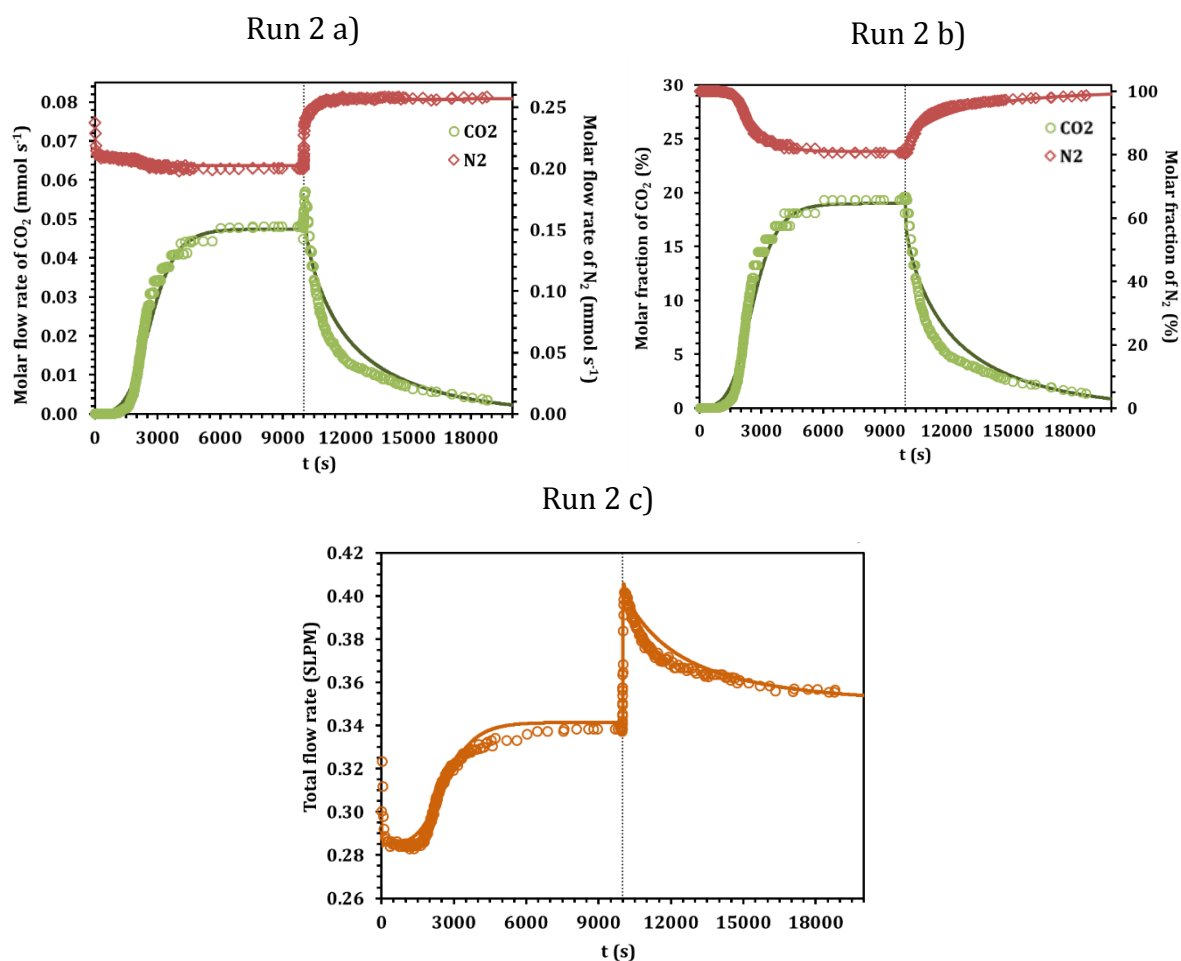
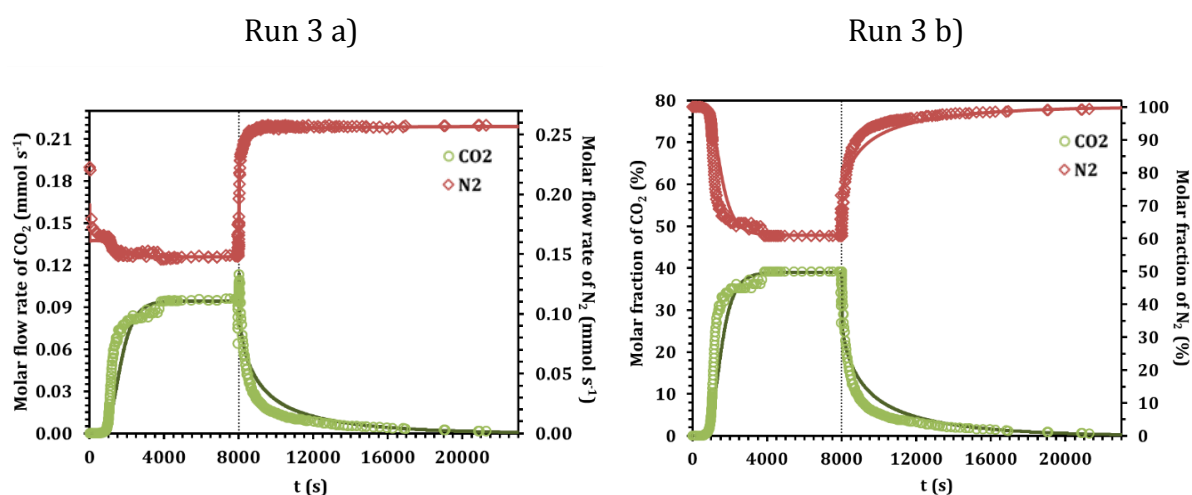


Figure 4.13. Breakthrough curve results of run 2 for inlet total pressure of 2.38 bar at 298 K: CO_2 and N_2 molar flow rate at the column outlet (a), CO_2 and N_2 molar fraction at the column outlet (b) and total flow rate at the column outlet (c). Points - experimental data; lines - model. Vertical line - beginning of desorption.



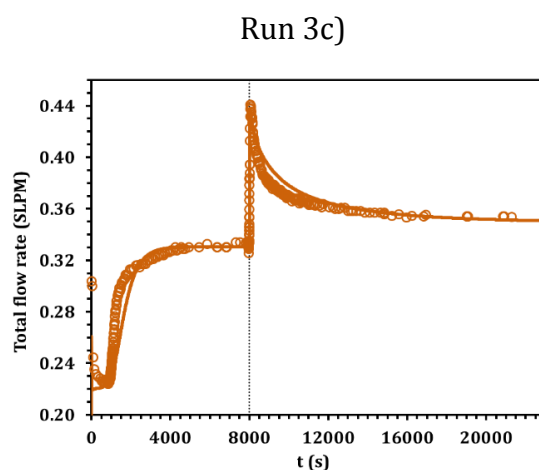


Figure 4.14. Breakthrough curve results of run 3 for inlet total pressure of 2.38 bar at 298 K: CO₂ and N₂ molar flow rate at the column outlet (a), CO₂ and N₂ molar fraction at the column outlet (b) and total flow rate at the column outlet (c). Points - experimental data; lines - model. Vertical line - beginning of desorption.

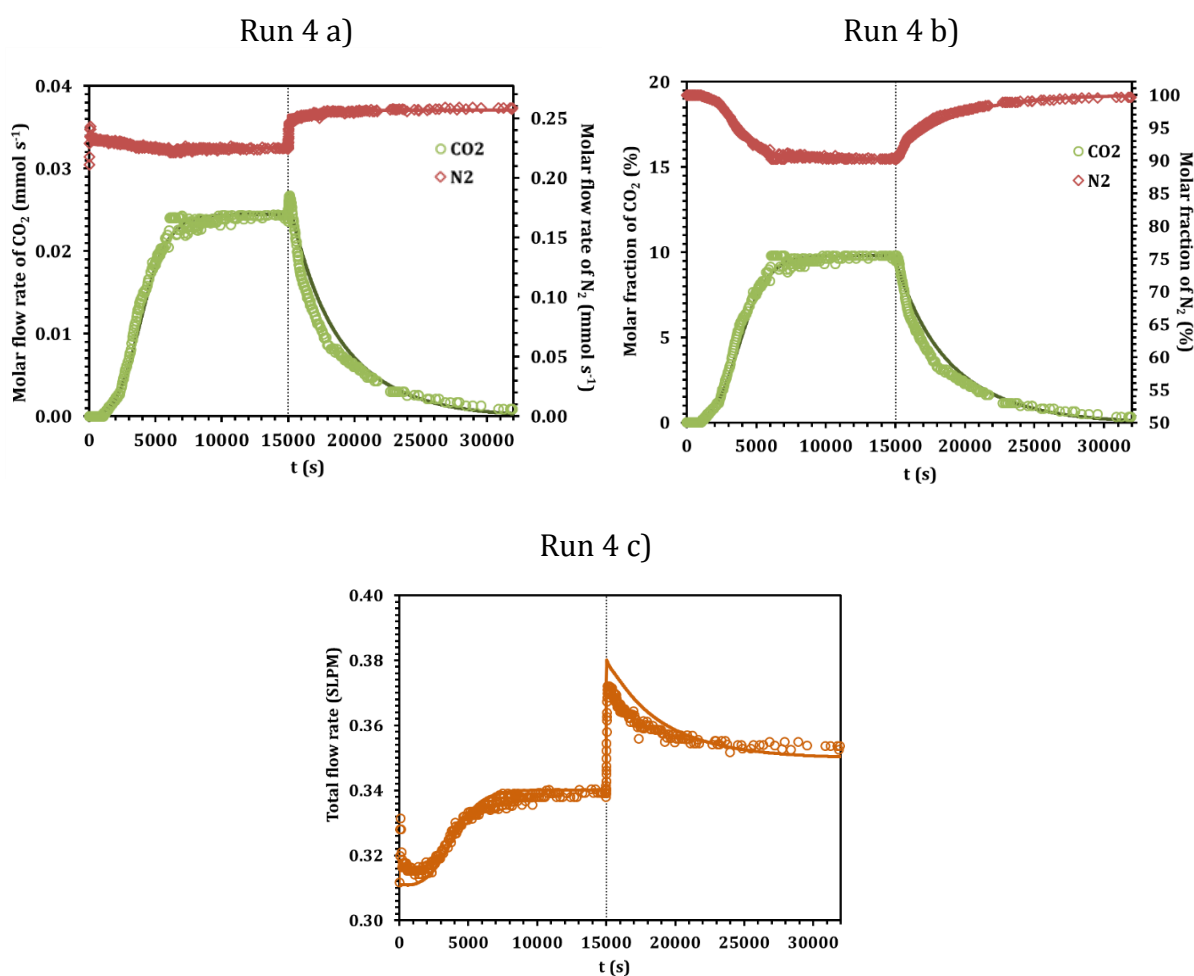


Figure 4.15. Breakthrough curve results of run 4 for inlet total pressure of 2.40 bar at 298 K: CO₂ and N₂ molar flow rate at the column outlet (a), CO₂ and N₂ fraction at the column outlet (b) and total flow rate at the column outlet (c). Points - experimental data; lines - model. Vertical line - beginning of desorption.

Run 1 corresponds to a single breakthrough curve of carbon dioxide in a column initially filled with helium. It can be observed that initially the CO₂ molar fraction at the outlet is zero, as it is being completely adsorbed in the monolith. Only He is exiting the column at a flowrate of approximately 0.240 SLPM which corresponds to the He being fed to the bed in addition to the He previously present in the bed that is being displaced by the feed mixture. At around 1400 s the CO₂ front starts to break through the bed, and of the outlet stream the CO₂ composition increases accompanied by an increase in the outlet total flow rate until a threshold is reached. This is indicative that equilibrium was achieved and that the adsorbent is saturated. At the beginning of desorption, a growth of flow rate is observed due to the release of the adsorbed gas and afterwards the flow starts to decrease until the end of the experiment. Due to the sharp nature of the CO₂ adsorption equilibrium isotherm, the desorption curve presents dispersive character and therefore a long time is required for complete regeneration of the bed, which is also predicted by the simulation. Runs 2, 3 and 4 correspond to binary breakthrough curves with three different feed streams in terms of CO₂ concentrations. Similar trends are observed for these experiments, initially no CO₂ exits the column and then the CO₂ molar fraction increases until the feed value together with the outlet flow rate. It can be seen that, as the CO₂ feed molar fraction increases, the breakthrough time decreases. Once again it is possible to verify a good agreement between experimental results and simulations for these three experiments. However, in these cases, at the beginning of experiments the column is filled with nitrogen and CO₂/N₂ mixtures are fed to the column. Therefore, multicomponent adsorption occurs and thus the multicomponent extension of the adsorption equilibrium is validated.

4.6 CONCLUSIONS

A new hybrid honeycomb monolithic material composed by 70% of 13X zeolite and 30% of activated carbon was developed by extrusion process.

Adsorption equilibrium isotherms of carbon dioxide and nitrogen on the honeycomb monolith were measured by gravimetric method using a Rubotherm[®] magnetic suspension balance in the temperature range between 303 and 373 K. Binary breakthrough experiments were carried out with different feed conditions in terms of carbon dioxide composition at 298 K and 2.40 bar, approximately. The extension of multicomponent Dual-Site Langmuir isotherm was used to predict the multicomponent

adsorption equilibrium. Also, in this case, a good agreement was obtained. The material presented a multicomponent equilibrium selectivity of 54.0 at 298 K, 2.40 bar and 10% CO₂ in N₂. A mathematical model was proposed and validated against the experimental breakthrough results.

Due to the high resistivity of this honeycomb monolith, breakthrough experiments with electrification in the desorption step and ESA cycles were not performed.

This property is an important characteristic to be taken into account in the next chapters.

NOMENCLATURE AND GLOSSARY

a_m	Area to volume ratio	m^{-1}
$b_{0,k,i}$	affinity constant at infinite temperature	bar^{-1}
$b_{k,i}$	affinity constant	bar^{-1}
C_{inlet}	inlet gas phase concentration	$mol \cdot m^{-3}$
C_i	gas phase concentration of component i	$mol \cdot m^{-3}$
C_p	heat capacity of the mixture at constant pressure	$J \cdot mol^{-1} \cdot K^{-1}$
$\widehat{C_p}$	heat capacity at constant pressure (per mass unit)	$J \cdot kg^{-1} \cdot K^{-1}$
$C_{p,i}$	heat capacity at constant pressure of component i	$J \cdot mol^{-1} \cdot K^{-1}$
$\tilde{C}_{p,s}$	solid specific heat (per mass unit)	$J \cdot kg^{-1} \cdot K^{-1}$
$\tilde{C}_{p,w}$	wall specific heat (per mass unit)	$J \cdot kg^{-1} \cdot K^{-1}$
C_s	concentration at the solid interface	$mol \cdot m^{-3}$
C_t	total gas phase concentration	$mol \cdot m^{-3}$
$\tilde{C}_{v,ads,i}$	molar specific heat of component i in the adsorbed phase at constant volume	$J \cdot mol^{-1} \cdot K^{-1}$
$C_{v,i}$	molar specific heat of component i at constant volume	$J \cdot mol^{-1} \cdot K^{-1}$
D	total diameter of channels	m
D_{ax}	mass axial dispersion coefficient	$m^2 \cdot s^{-1}$
$D_{k,i}$	Knudsen diffusivity of component i	$m^2 \cdot s^{-1}$
D_m	molecular diffusivity	$m^2 \cdot s^{-1}$
$D_{m,i}$	molecular diffusivity of component i	$m^2 \cdot s^{-1}$
e	column wall thickness	m
h_f	heat transfer coefficient between the gas and the particle	$W \cdot m^{-2} \cdot K^{-1}$
h_w	heat transfer coefficient between the gas phase and the wall	$W \cdot m^{-2} \cdot K^{-1}$
k_g	thermal conductivity of the gas mixture	$W \cdot m^{-2} \cdot K^{-1}$
$k_{g,i}$	thermal conductivity of component i	$W \cdot m^{-2} \cdot K^{-1}$
k_f	film mass transfer coefficient	$m \cdot s^{-1}$
k_{macro}	LDF coefficient for macropores	s^{-1}
k_{micro}	LDF coefficient for micropores	s^{-1}
L_c	Monolith length	m
l_w	monolith wall thickness	m
m_s	adsorbent mass	kg

M_w	adsorbate molecular weight	$\text{kg}\cdot\text{mol}^{-1}$
P	Pressure	bar
P_i	Partial pressure of component i	bar
Pr	Prandtl number	-
q_i	adsorbed amount of component i	$\text{mol}\cdot\text{kg}^{-1}$
$\bar{q}_i$	particle average adsorbed concentration	$\text{mol}\cdot\text{kg}^{-1}$
q_i^*	adsorbed concentration in equilibrium of component i	$\text{mol}\cdot\text{kg}^{-1}$
$q_{sat,i}$	adsorbent saturation capacity of component i	$\text{mol}\cdot\text{kg}^{-1}$
Re	Reynolds number	-
R_g	universal gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
R_c	equivalent monolith radius (approximation of cylindrical monolith)	m
$R_{ch,e}$	equivalent channel radius (approximation of cylindrical channel)	m
Sc	Schmidt number	-
Sh	Sherwood number	-
T	Temperature	K
T_g	temperature of the gas phase	K
T_{inlet}	inlet temperature	K
T_s	temperature of the solid phase	K
T_w	wall temperature	K
T_∞	external temperature	K
u_0	superficial gas velocity	$\text{m}\cdot\text{s}^{-1}$
u_m	Interstitial gas velocity	$\text{m}\cdot\text{s}^{-1}$
U	overall heat transfer coefficient	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
V_C	volume of the permanent magnet, of the sample basket and of the glass wool used to hold the sample	$\text{m}^3\cdot\text{mol}^{-1}$
V_S	volume of the solid adsorbent	$\text{m}^3\cdot\text{mol}^{-1}$
y_i	molar fraction of component i	-
z	axial position	m

GREEK LETTERS

α_w	Ratio of the internal surface area to the volume of the column wall	m^{-1}
α_{wl}	Ratio of the log mean surface area to the volume of the column wall	m^{-1}
ΔH	Heat of adsorption	$\text{kJ}\cdot\text{mol}^{-1}$
ΔH_i	Isosteric heat of adsorption of component i	$\text{kJ}\cdot\text{mol}^{-1}$
ε	Bed porosity	-
ε_p	particle porosity	-
λ	Heat axial dispersion coefficient	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
μ	Fluid viscosity	$\text{Pa}\cdot\text{s}$
ρ	Gas density	$\text{kg}\cdot\text{m}^{-3}$
ρ_{ap}	Apparent density	$\text{kg}\cdot\text{m}^{-3}$
ρ_b	Bulk density	$\text{kg}\cdot\text{m}^{-3}$
ρ_w	Wall density	$\text{kg}\cdot\text{m}^{-3}$

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5 PELLETS WITH ZEOLITE AND ACTIVATED CARBON BY EXTRUSION PROCESS

In this chapter, it is reported the production of four types of pellets with different amounts of zeolite 13X and activated carbon by extrusion. An extensive study of the viability of these adsorbents, in terms of adsorption capacity, electrical conductivity and shaping for the main objective of the work, i.e., their application in ESA process, was developed.

5.1 PELLETS PRODUCTION

Four types of pellets were produced with different amounts of zeolite 13X and activated carbon. The pellets were produced by extrusion process based on the detailed description of this process presented in section 3.3 of Chapter 3.

The first experiments performed were used to identify the quantity of water needed for each type of pellet, the quantity of binder and the parameters related with the shaping process, such as time for powders (dry and wet) mixing, as well as the respective speed of the blades, and also screw speed during the extrusion. The first experiments were rejected because the obtained pellets did not have a homogeneous aspect, or the hardness was too low, and they broke easily.

After some tests, four types of pellets were extruded. Table 5.1 reports the amount of raw materials, binder and water used to produce the four types of pellets. These pellets will be referred to considering the amount of zeolite 13X and activated carbon present in their composition. Pellets produced with activated carbon only, i.e., without zeolite 13X, were named “100%AC”, “70%AC-30%13X”, “50%AC-50%13X” and “30%AC-70%13X” were used to define the other pellets with the two raw materials (activated carbon and zeolite 13X), in which the percentage corresponds to the amount of each raw material present.

Table 5.1. Amount of raw materials, binder and water used in the preparation of the extruded pellets.

Pellets	Weight of components (g)			Volume of water (mL)
	13X	AC	CMC	
100% AC	0	20.132	1.021	39
70%AC-30%13X	9.085	20.939	1.539	21
50%AC-50%13X	7.477	7.469	0.740	13
30%AC-70%13X	10.487	4.500	0.753	12

Zeolite powder G5 XP (13X), supplied by CECA Arkema Group, and Maxsorb G08H powder, supplied by Kansai Coke & Chemicals, were used as raw materials for 50%AC-50%13X and 30%AC-70%13X pellets production. Zeolite 13X (Kostrolith NaMSX P-TR, Chemiewerk) and Maxsorb MSC-30 (Kansai Coke and Chemicals Co, Ltd.) were used to produce the 70%AC-30%13X pellets. Maxsorb MSC-30 was also used to produce the pellets with 100% of activated carbon. Carboxymethylcellulose was used in all experiments as organic binder, and it was provided by VWR Chemicals.

The powders of the adsorbent materials and binder were mixed at 60-65 rpm in the mixing chamber. After 30 min of dry mixing, water was added, drop by drop, at 80 rpm during 30 min. When a wet paste with homogeneous aspect was formed, it was manually fed from the feed tray and dropped down a vertical feed tube onto the screw through a circular aperture in the auger tube, as described in section 3.3 of Chapter 3. The material was compressed and extruded through the die with holes of 2 mm of diameter. After that, the extrudates were dried for 24 hours at room temperature. Finally, the extrudates were broken into small pellets (length between 3 and 5 mm).

Figure 5.1 shows the four types of pellets produced.

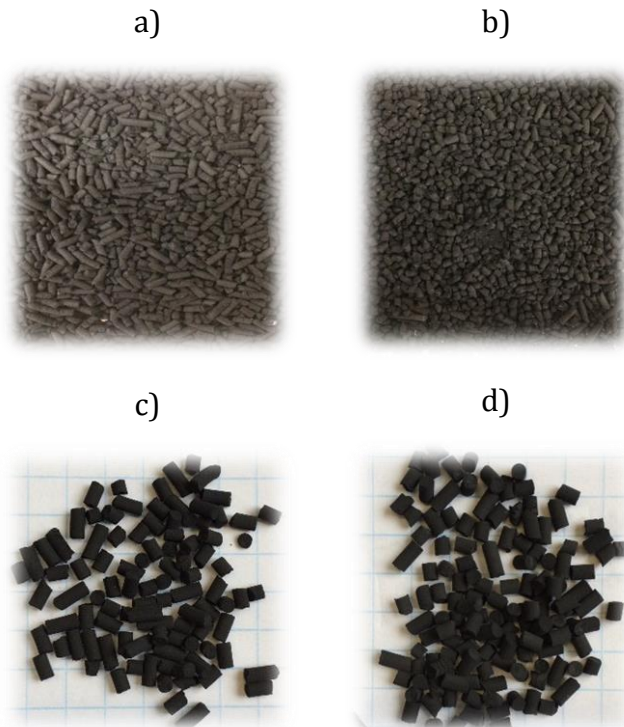


Figure 5.1. Pellets produced by extrusion: a) 100%AC; b) 70%AC-30%13X; c) 50%AC-50%13X; d) 30%AC-70%13X.

5.2 CHARACTERIZATION

5.2.1 N₂ ISOTHERM AT 77 K

All samples were characterized following the description in section 3.6.2 Chapter 3. Before characterization, the sample of Maxsorb raw material and the 100%AC pellets were activated in helium at 473 K, while the other materials, 70%AC-30%13X, 50%AC-50%13X, 30%AC-70%13X pellets and zeolite 13X powder were activated in helium at 573 K.

Figure 5.2 to Figure 5.7 a) present the curves of N₂ adsorption and desorption isotherms at 77 K obtained for the six samples: Maxsorb MSC-30 powder raw material, 100% AC pellets, 70%AC-30%13X pellets, 50%AC-50%13X pellets, 30%AC-70%13X pellets and zeolite 13X powder raw material (Chemiewerk), respectively.

Figure 5.2 to Figure 5.7 b) present the pore size distribution of these six different samples, in the same order, calculated from the adsorption branches of the nitrogen isotherm at 77 K. The pore size distribution was determined using Density Functional Theory (DFT).

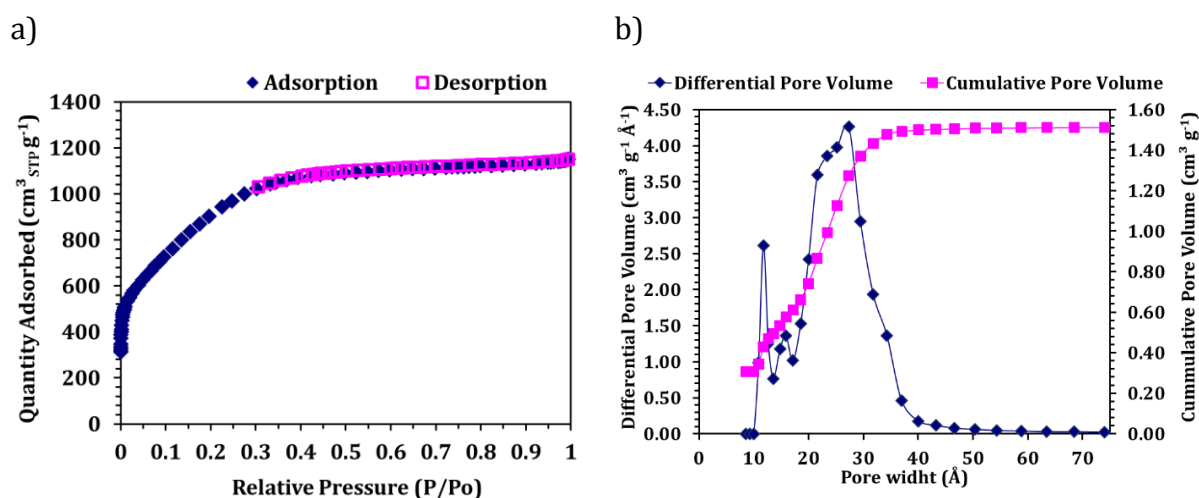


Figure 5.2. Results of a) nitrogen adsorption isotherm at 77 K on Maxsorb raw material (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution calculated from the adsorption branch of the nitrogen isotherm at 77 K by the DFT method.

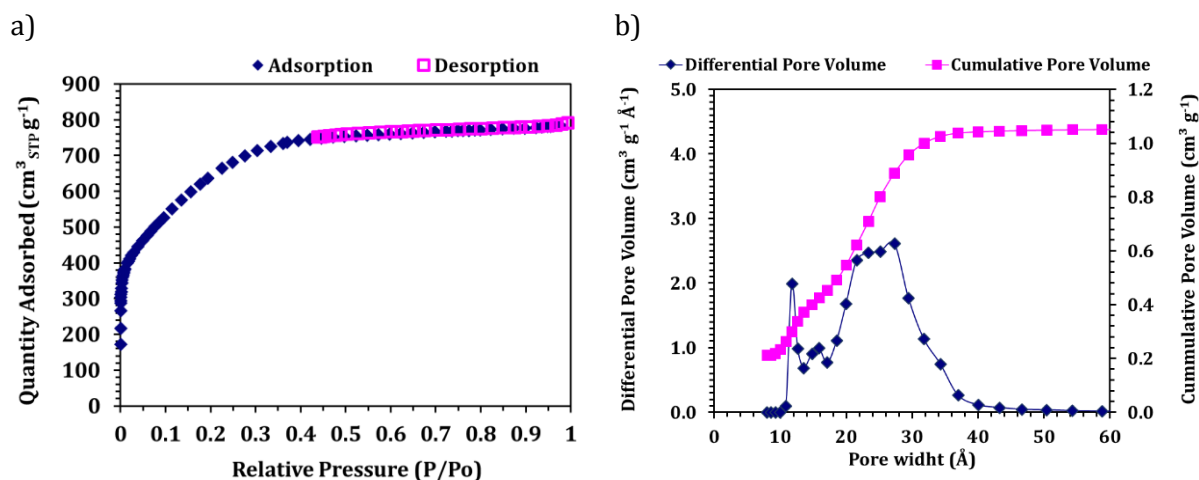


Figure 5.3. Results of a) nitrogen adsorption isotherm at 77 K on 100%AC pellets at 77 K (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution calculated from the adsorption branch of the nitrogen isotherm at 77 K by the DFT method.

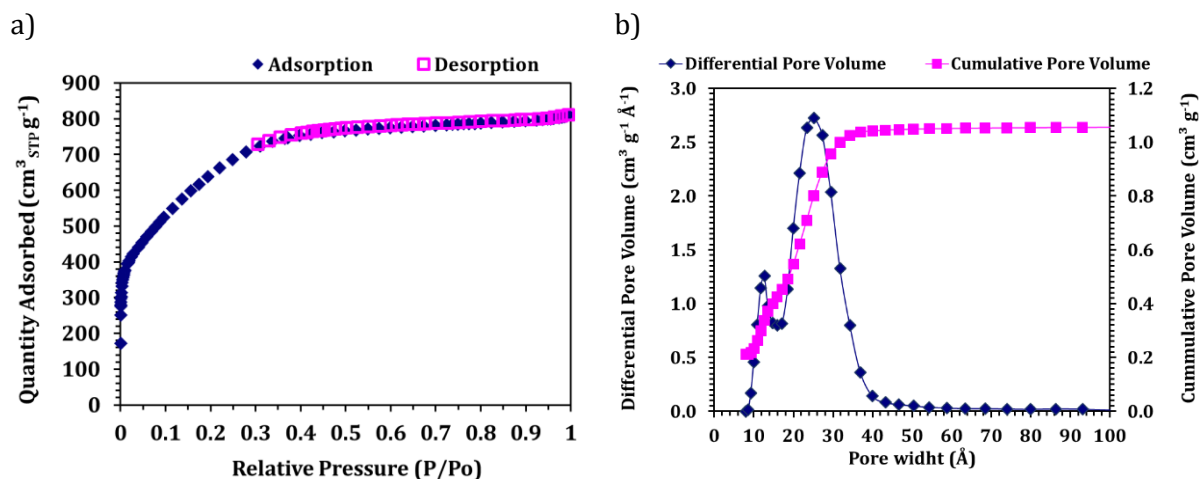


Figure 5.4. Results of a) nitrogen adsorption isotherm at 77 K on 70%AC-30%13X pellets at 77 K (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution calculated from the adsorption branch of the nitrogen isotherm at 77 K by the DFT method.

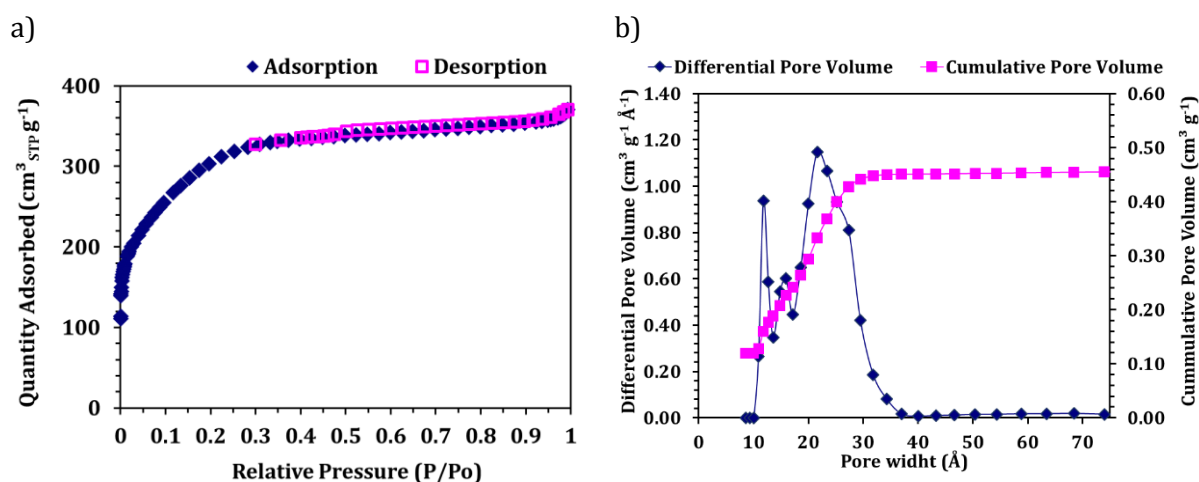


Figure 5.5. Results of a) nitrogen adsorption isotherm at 77 K on 50%AC-50%13X pellets at 77 K (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution calculated from the adsorption branch of the nitrogen isotherm at 77 K by the DFT method.

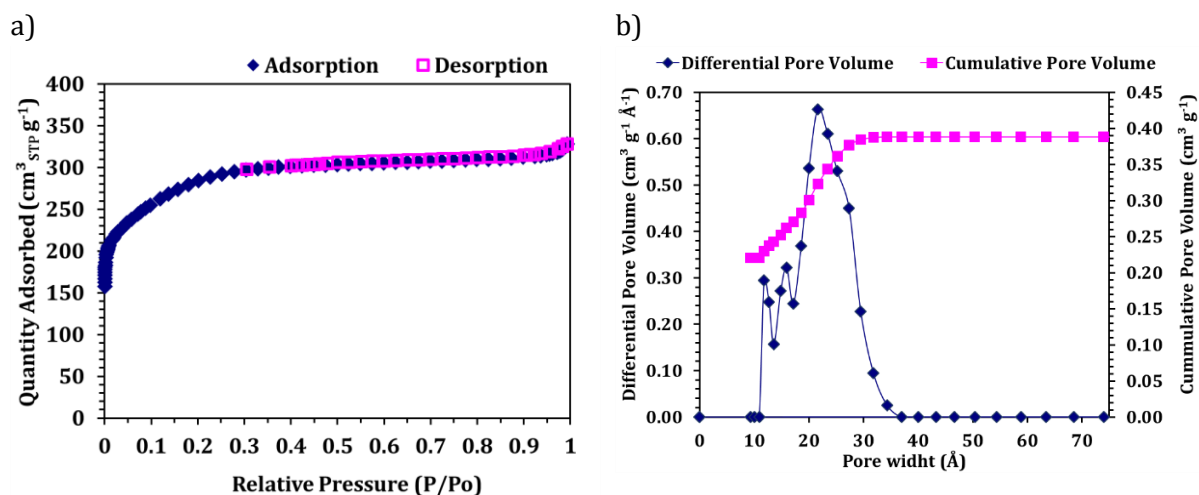


Figure 5.6. Results of a) nitrogen adsorption isotherm at 77 K on 30%AC-70%13X pellets at 77 K (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution calculated from the adsorption branch of the nitrogen isotherm at 77 K by the DFT method.

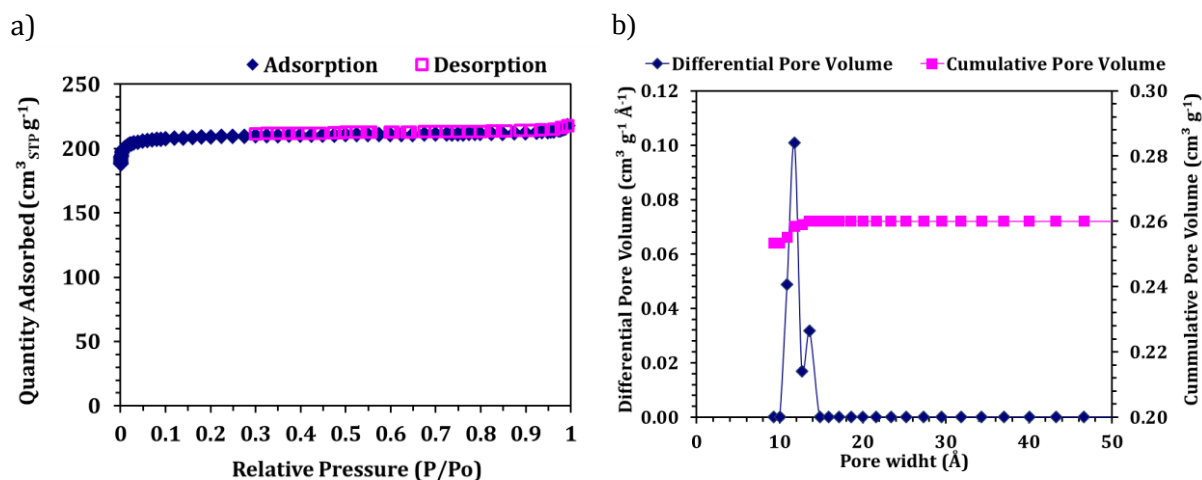


Figure 5.7. Results of a) nitrogen adsorption isotherm at 77 K on zeolite 13X raw material at 77 K (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution calculated from the adsorption branch of the nitrogen isotherm at 77 K by the DFT method.

In order to compare the results of the nitrogen adsorption equilibrium isotherms at 77 K, results presented in the above figures a) are given together in Figure 5.8.

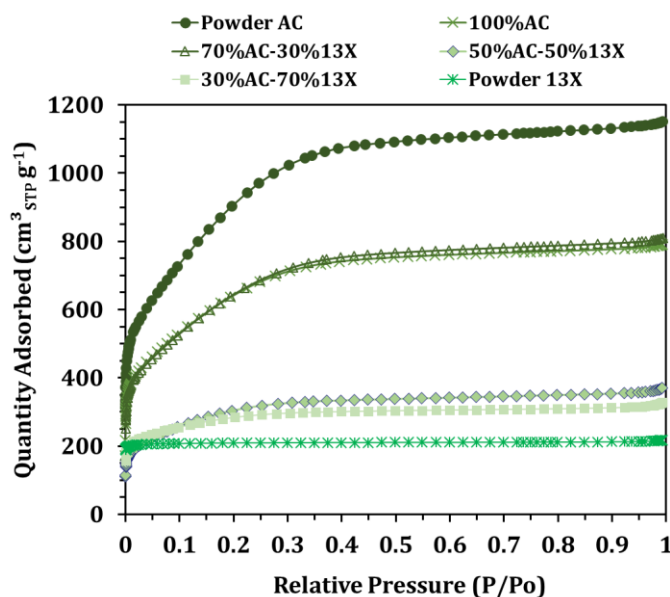


Figure 5.8. Comparison between the results of nitrogen adsorption isotherm at 77 K on Maxsorb powder (circles), 100%AC pellets (crosses), 70%AC-30%13X pellets (triangles), 50%AC-50%13X pellets (diamonds), 30%AC-70%13X pellets (squares) and 100%13X powder (asterisks).

Observing the results of the N₂ isotherms at 77 K for all materials, it is evident that all isotherms show a type I behaviour, according to the IUPAC definition.

Until relative pressures of about 0.1, an increase of volume adsorbed is evident for the samples Maxsorb powder raw material (Figure 5.2 a)), 100%AC (Figure 5.3 a)) and 70%AC-30%13X (Figure 5.4 a)), which suggests a large amount of micropores in the samples. Above 0.7 of relative pressure, practically all samples present the same type of behaviour, except zeolite 13X, in which the pores are smaller and it is not verified any difference in the adsorbed amount in this range of pressures. Comparing adsorption and desorption (open points) isotherms, it can be seen that hysteresis was not verified for all samples.

Figure 5.2 to Figure 5.6 b) indicate a range of pore widths between 10 and 40 Å, while Figure 5.7 shows a pore width between 10 to 12 Å, i.e., a very narrow distribution was observed, corresponding to the microporous characteristic of zeolites. Figure 5.2 b), which corresponds to the activated carbon, presents the wider size distribution, between 20 and 40 Å, followed by 70%AC-30%13X (Figure 5.4 b)), 50%AC-50%13X (Figure 5.5 b)) and 30%AC-70%13X (Figure 5.6 b)), as expected due to the decrease of activated carbon amount in the samples. The results confirmed the presence of mesoporosity in the activated carbon. It can also be seen from the cumulative pore volume results, that the total pore volume values decrease as the amount of activated carbon decrease (Figure 5.2 b) to Figure 5.6 b)), also confirming that the mesoporosity of sample decreases and microporosity increases due to the higher quantity of zeolite.

5.2.2 CO₂ ISOTHERM AT 273 K

Figure 5.9 a) to f) present the CO₂ adsorption isotherms at 273 K for all pellets and powders raw materials.

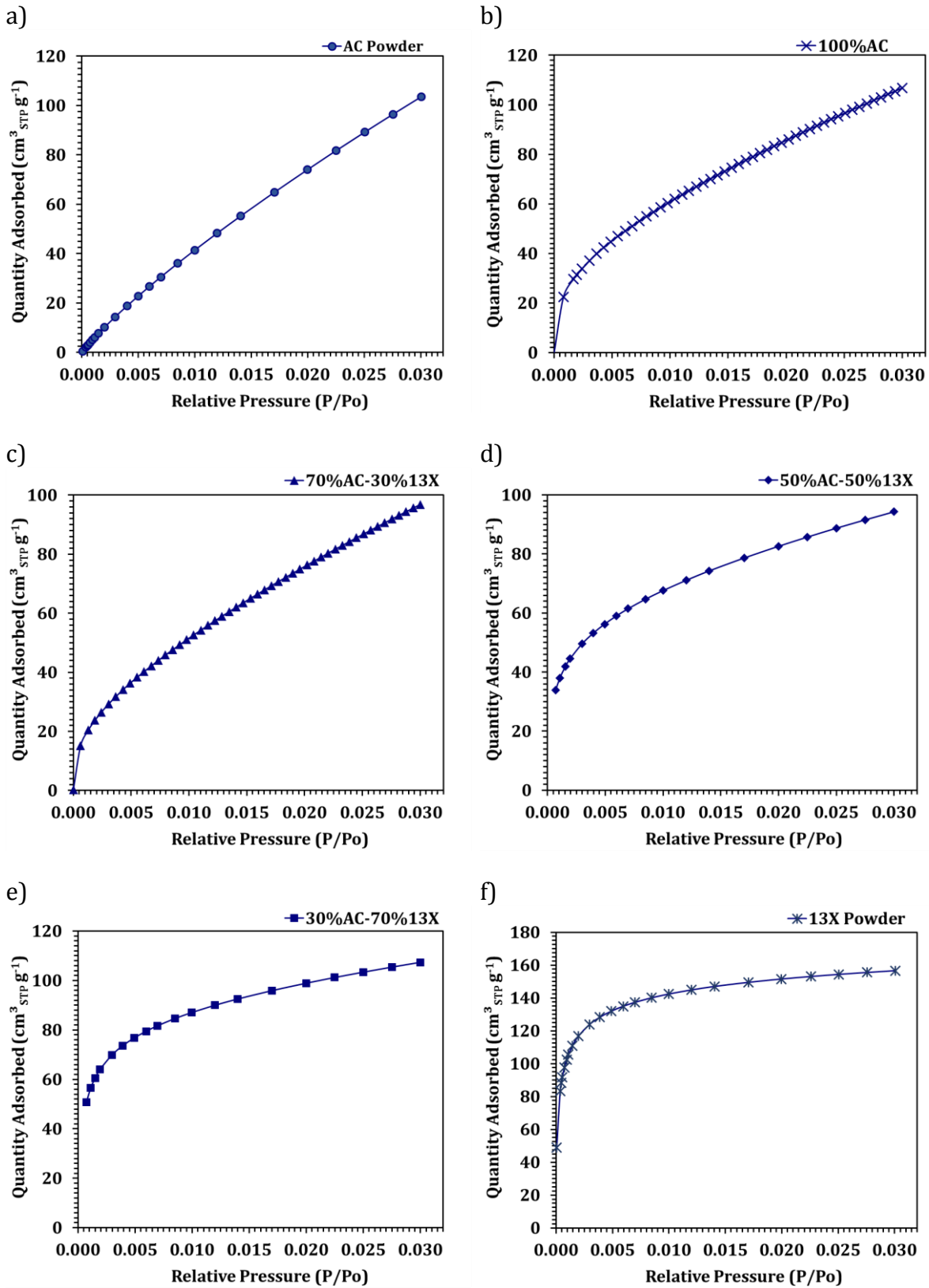


Figure 5.9. Results of the CO₂ adsorption isotherm at 273 K of Maxsorb raw material (a), 100%AC pellets (b), 70%AC-30%13X (c), 50%AC-50%13X (d), 30%AC-70%13X (e), zeolite 13X powder (f).

Figure 5.10 shows the comparison between all CO₂ isotherms at 273 K.

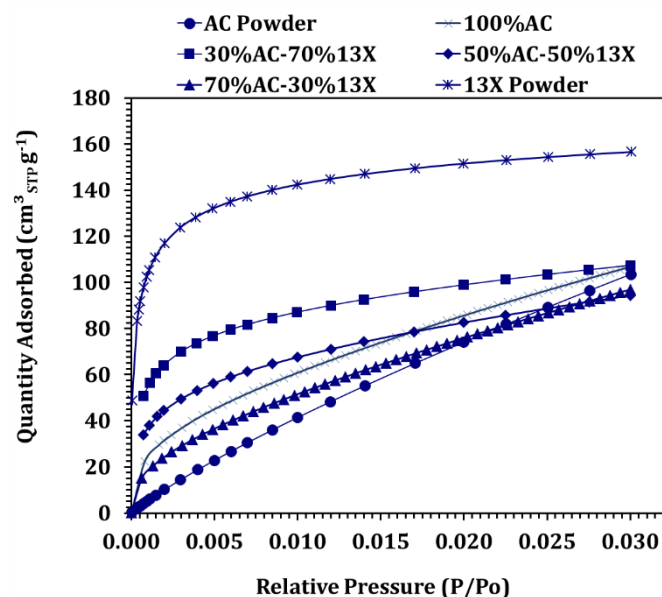


Figure 5.10. Comparison between the results of the CO₂ adsorption isotherm on Maxsorb raw material (circles), 100%AC pellets (crosses), 70%AC-30%13X pellets (triangles), 50%AC-50%13X pellets (diamonds), 30%AC-70%13X pellets (squares), 13X zeolite powder (asterisks) at 273 K.

This type of characterization allows access to information on small pores [1]. As can be seen, for all the samples analysed, the isotherms show a characteristic behaviour of type I isotherm, in general observed in microporous materials and with the possibility of narrow mesoporous. As expected, zeolite 13X raw material presented the high CO₂ adsorbed amount, followed by 30%AC-70%13X pellets, and by 50%AC-50%13X pellets at low relative pressures. Also, for high pressures, the behaviour observed was different because of the large amount of mesopores, due to the increase of activated carbon quantity, which implies an increase of CO₂ adsorbed as the relative pressure increases.

5.2.3 MERCURY INTRUSION POROSIMETRY

Figure 5.11 a) to d) presented the results of mercury porosimetry for the four types of pellets produced.

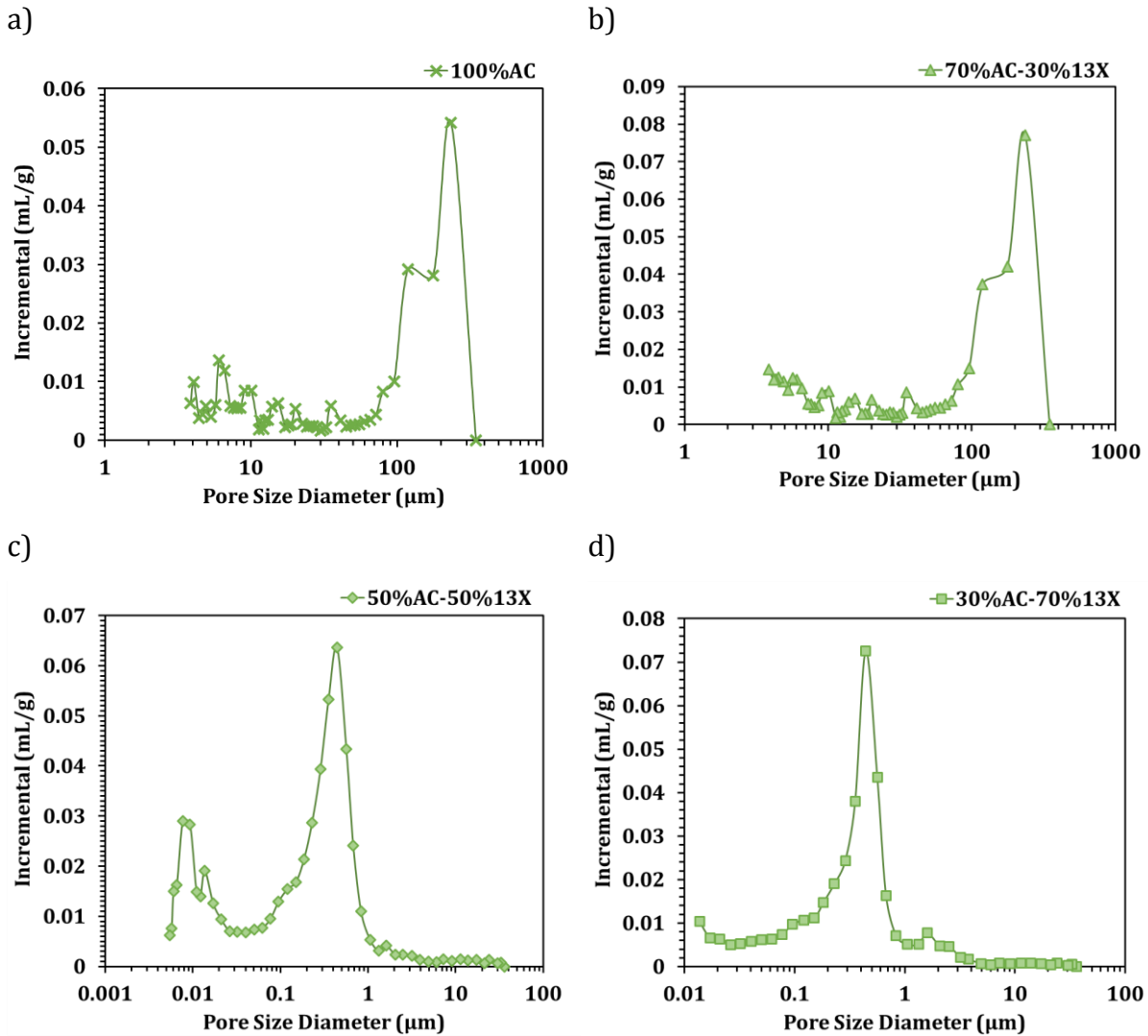


Figure 5.11. Results of incremental intrusion volume of mercury on a) 100%AC pellets (crosses); b) 70%AC-30%13X pellets (triangles); c) 50%AC-50%13X pellets (diamonds); d) 30%AC-70%13X pellets (squares).

In Figure 5.11 a) and b), an evident range pore width between 100 μm and 300 μm, approximately, was observed, due to the presence of larger pores in activated carbon. When the amount of zeolite 13X increases in the composition of pellets, the range of pores diameter was clearly lower, between 0.1 and 1 μm, approximately, i.e., 1000 times lower, as observed in Figure 5.11 c) and d).

The main results obtained from textural characterization are summarised in Table 5.2.

Table 5.2. Surface area and pore structure parameters for all materials.

Sample/Parameter	Maxsorb Powder	100%AC	70%AC-30%13X	50%AC-50%13X	30%AC-70%13X	13X Powder
Surface area (m ² g ⁻¹)	3371 ^a 2982 ^c	2353 ^a 2124 ^c	2378 ^a 2126 ^c	1118 ^a 1036 ^c	1011 ^a 964 ^c	916 ^b 910 ^c
Pore diameter (nm)	-	1372 ^d 47.2 ^e	1314 ^d 49.2 ^e	237 ^d 27.8 ^e	334 ^d 35.4 ^e	-
Apparent Density (kg m ⁻³)	-	861	901	1307	1444	-
Porosity	-	0.571	0.613	0.444	0.379	-

^a Surface area (S) determined by BET (Brunauer-Emmett-Teller) method
^b Surface area (S) determined by Langmuir method
^c t-Plot micropore area
^d Median Pore diameter (volume - determined by Hg porosimetry)
^e Average pore diameter calculated by $4V_{\text{TOTAL}}/\text{Area}$ (determined by Hg porosimetry assuming cylinder pores)

The first line of Table 5.2 represents the estimated surface area of each sample. The surface area can be estimated by several methods, such as, Brunauer-Emmett-Teller (BET) method, Langmuir method and t-plot. It is observed a trend of decrease on the surface area value as the amount of zeolite increases.

The pore diameters presented in the second line were determined by mercury porosimetry. The first ones correspond to a median pore diameter estimated by volume. The second ones are the average pore diameters estimated through the ratio between total intrusion volume and total pore area, considering pores with a cylinder shape.

The 100%AC pellets presented the smaller value of apparent density followed by the pellets 70%AC-30%13X, 50%AC-50%13X and 30%AC-70%13X. Also, it can be seen that with the increase of zeolite quantity, the porosity values in generally decrease.

5.2.4 THERMOGRAVIMETRIC ANALYSIS

Figure 5.12 shows the TGA curves obtained under air for the raw materials, for carboxymethylcellulose, and for two types of pellets developed: 50%AC-50%13X and 30%AC-70%13X. It should be noticed that the powder samples (CMC, AC and 13X zeolite)

were tested as received (i.e. without any previous activation), while the pellet samples were tested after activation at 300 °C in helium.

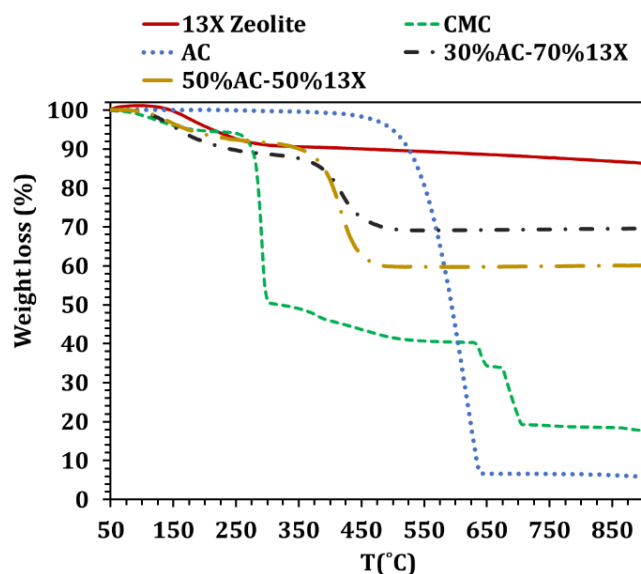


Figure 5.12. TGA curves of the materials used obtained under air flow: 13X zeolite (red line), activated carbon (blue points), CMC (green dashed line), 50%AC-50%13X pellets (yellow long dashed line) and 30%AC-70%13X pellets (black small dashed line).

According to Figure 5.12 up to approximately 300 °C, it is observed only about 7% and 10% of total mass decrease in CMC and zeolite 13X samples, respectively, while in activated carbon, it was not verified any loss (only 0.5% of the mass was lost until 100 °C). After that, between 300 °C and 650 °C, about 62% of volatiles are burned in CMC, and the total weight loss until 900 °C was about 77.3% of volatiles. In terms of activated carbon sample, burning started at 450 °C and lasted until 630 °C, approximately, corresponding to a 94.2% of volatiles burned. It was verified that zeolite 13X is the most stable material, demonstrated by the small quantity of volatiles burned in the experiment (about 12.5%). The volatiles burned in the 50%AC-50%13X pellets were higher than the ones burned in the 30%AC-70%13X pellets, due to the higher quantity of activated carbon, values of 39.3% and 29.8% were estimated, respectively.

No marked differences were observed on the thermal stability from 630 °C to 900 °C, and the remaining mass at this temperature corresponded to the zeolite fraction of the samples. The behaviour observed in this work is in the line of the results reported for other materials containing activated carbon and/or zeolite as raw materials [2-5].

Table 5.3 reports the percentage of water, volatiles burned, fixed carbon and ashes in the samples represented in Figure 5.12.

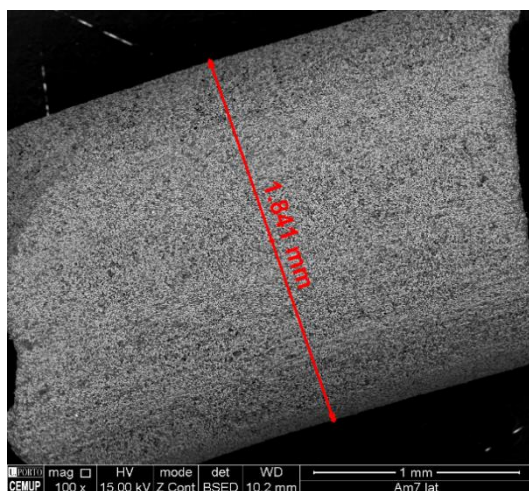
Table 5.3. Percentages of humidity, volatiles, fixed carbon and ashes for samples of zeolite 13X, activated carbon, CMC, 50%AC-50%13X and 30%AC-70%13X.

Sample	% H ₂ O	% Volatiles	% Fixed Carbon	% Ash
Zeolite 13X	1.2	12.5	1.2	85.1
Maxsorb AC	0	94.2	1.8	4.0
CMC	1.1	77.3	1.5	20.1
50%AC-50%13X	0.5	39.3	0	60.2
30%AC-70%13X	0.5	29.8	0	69.7

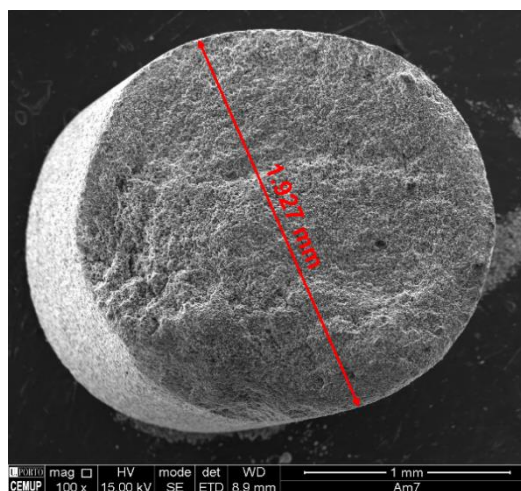
5.2.5 SEM/EDS ANALYSIS

The pellets morphology was investigated by SEM micrographs. As the expected results are similar for all pellets produced, varying only in terms of density of activated carbon and zeolite, SEM/EDS analyses were carried out only for one type of pellets (30%AC-70%13X). The results are given in Figure 5.13 , presenting in a) an image of the surface of a pellet, in b) a transversal cut of a pellet, in c) and in d) an amplification of the interior of the sample (1000× and 10000×), and in e) and in f) the energy dispersive spectrum of two zones (1 and 2 of d), respectively.

a)



b)



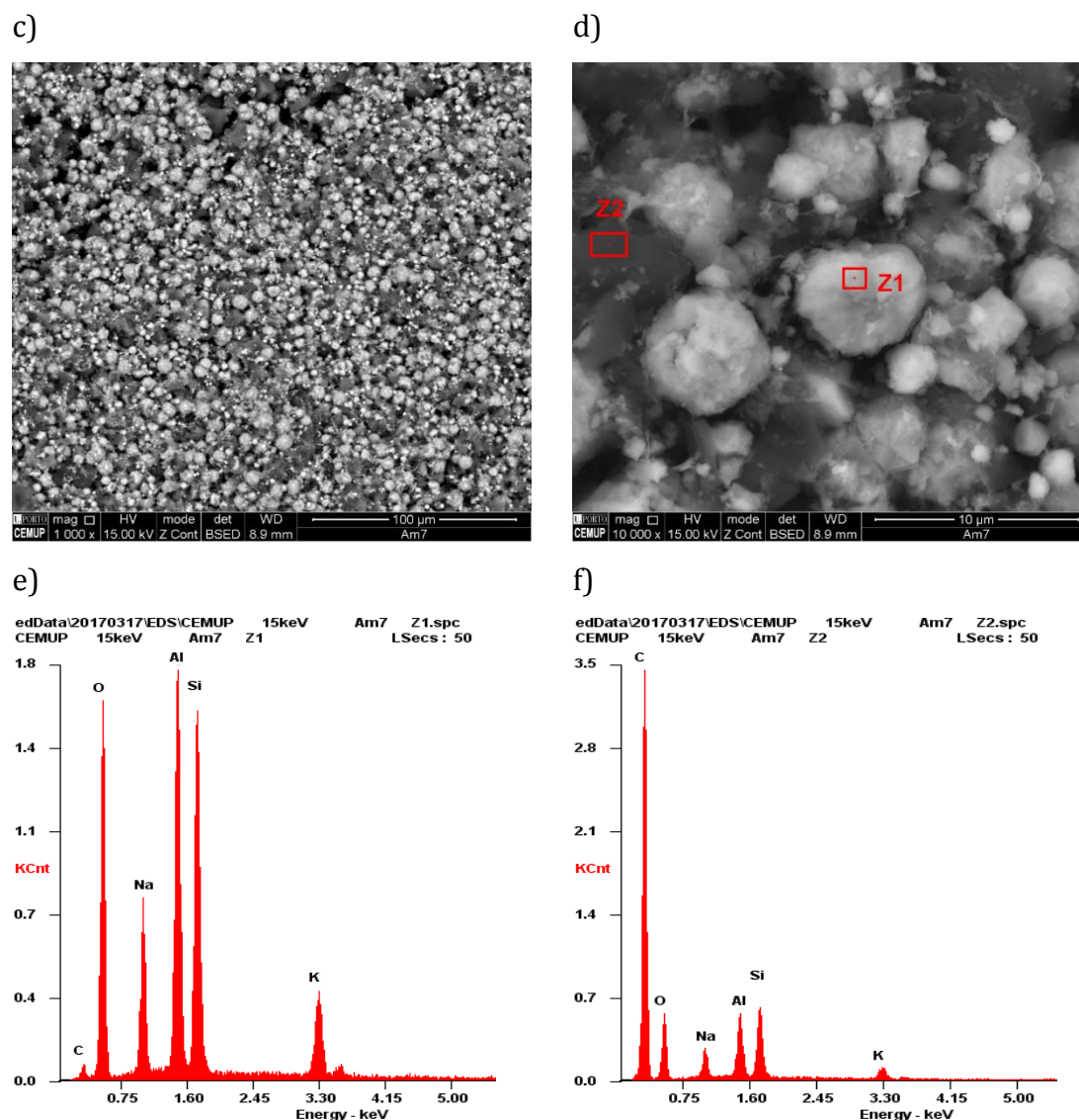


Figure 5.13. a) SEM photograph of the surface of a 30%AC-70%13X pellet with indication of the diameter dimension; b) SEM photograph of the interior of a 30%AC-70%13X pellet with indication of the diameter dimension; c) fragment of a 30%AC-70%13X pellet $\times 1000$ magnification; d) fragment of a 30%AC-70%13X pellet $\times 10000$ magnification; e) EDS spectra from analysis of zone 1 of d); f) EDS spectra from analysis of zone 2 of d).

Figure 5.13 a) and b) allowed to estimate the pellet diameter (approximately 1.9 mm) and to observe the surface and the interior of a pellet, respectively. Figure 5.13 c) and d) demonstrated a large amount of zeolite crystals and large portions of activated carbon. The distribution of both materials is apparently homogeneous.

Figure 5.13 e) represents the zone 1 (portion of zeolite 13X), revealing the presence of oxygen (O), sodium (Na), aluminium (Al), silicon (Si) and potassium (K), characteristic elements of zeolite 13X. In zone 2 (part of activated carbon), carbon (C) and oxygen (O)

were the elements present in higher quantity, as expected, as the main elements of activated carbon.

5.2.6 MECHANICAL STRENGTH

Single particle axial crushing strength tests were performed on two samples according to the description presented in section 3.6.9 of Chapter 3: 100%AC pellets and 30%AC-70%13X pellets. In these tests, the maximum compressive strength before failure was measured for 50 pellets of each sample. The results obtained are reported in Figure 5.14 a) and b), and in Table 5.4, summarizing the results in terms of number of particles tested, strength average, minimum and maximum values and standard deviation of the results, in Newton.

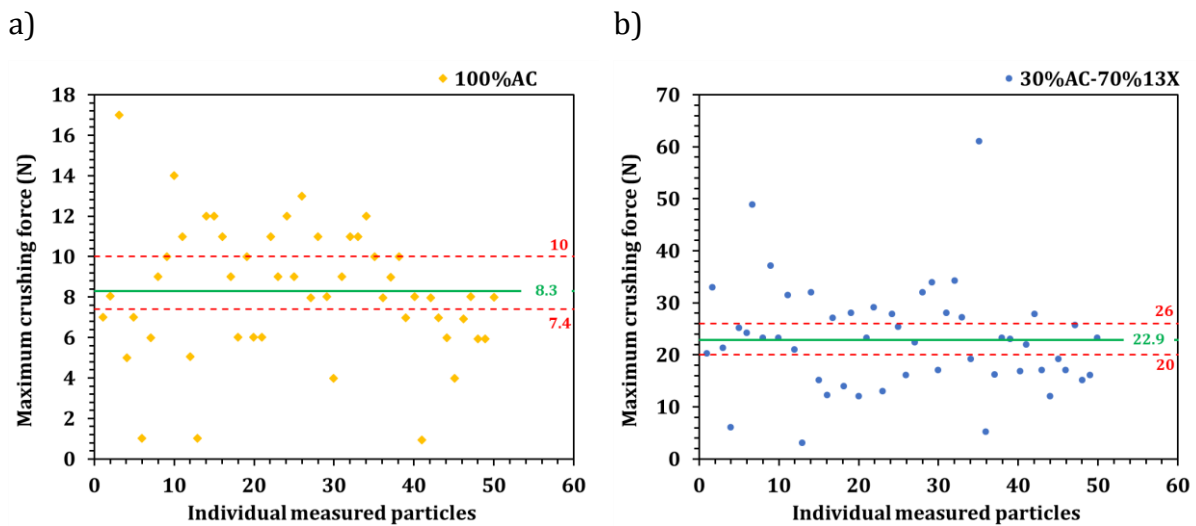


Figure 5.14. Maximum crushing strength measured for 50 pellets of a) 100%AC and b) 30%AC-70%13X.

Table 5.4. Summary of the results obtained for 50 pellets in mechanical strength tests of 100%AC pellets and 30%AC-70%13X pellets.

Parameter (N)	100%AC	30%AC-70%13X
Crushing strength average	8.3	22.9
Standard deviation	3.2	10.2
Minimum value	1	3
Maximum value	17	61

Considering that each pellet has a size between 3 and 5 mm of length (average value of 4 mm used for calculation) and a diameter of about 1.9 mm, as verified in SEM analyses (these pellets were not analysed in SEM, but the same die was used during extrusion process, then the same diameter was considered), the cross section considered was of 1.9 × 4 mm, approximately. The results obtained were about 8.3 N (0.73 MPa) and 22.9 N (2.02 MPa) for 100%AC pellets and 30%AC-70%13X pellets, respectively.

Observing the results obtained, it is possible to conclude that the 30%AC-70%13X pellets have clearly high strength than the 100%AC pellets. In fact, the quantity of binder used in these two types of pellets was practically the same, meaning that in order to have the same mechanical strength the pellets only with activated carbon would require more binder.

In literature, Tepamat *et al.* (2014) [6] reported the production of pellets of rectangular shape with 10 mm width, 60 mm length and 10 mm thickness by hydraulic pressing at 60 MPa using a mixture between carbon and zeolite NaA as raw materials plus 5-20% of phenolic resin and 1% of carboxymethylcellulose as binders. The materials produced showed a mechanical strength of 0.68 MPa. This value is in the order of magnitude of the values obtained for the pellets produced in this work.

5.3 MATHEMATICAL MODEL

To describe the dynamic behaviour of single or multicomponent adsorption in the fixed bed, material, energy and momentum balances were written. The following assumptions were considered [7, 8]:

- Ideal gas behaviour;
- Constant porosity along the bed;
- No mass, heat or velocity gradients in the radial dimension;
- Internal mass transfer resistance described with the Linear Driving Force (LDF) equation;
- Absence of temperature gradients inside the adsorbent, since the heat transfer in the solid is much faster than in the gas phase;
- Axial dispersed plug flow;
- The Ergun equation is valid locally, i.e., in the momentum balance, only the terms of pressure drop and velocity change are considered.

The material balance for each component in the gas phase is given by equation 5.1:

$$\frac{\partial}{\partial z} \left(\varepsilon_b D_{ax} C_{gt} \frac{\partial y_i}{\partial z} \right) - \frac{\partial}{\partial z} (u_0 C_{gi}) - \varepsilon_b \frac{\partial C_{gi}}{\partial t} - (1 - \varepsilon_b) a_p k_f (C_{gi} - C_{si}) = 0 \quad 5.1$$

where z is the axial position, t is the time, ε_b is the bed porosity, u_0 is the superficial velocity, C_{gt} and C_{gi} are respectively the total and component i gas phase concentrations, y_i is the molar fraction of component i , C_{si} is the concentration of component i at the solid interface, D_{ax} is the mass axial dispersion coefficient, k_f is the film mass transfer coefficient and a_p is the particle external specific area.

In the momentum balance, the forces acting in a reference control volume are described. Considering only the terms of pressure drop and velocity change, which are related through the Ergun equation, the momentum balance is defined by equation 5.2:

$$-\frac{\partial P}{\partial z} = \frac{150 \mu_g (1 - \varepsilon_b)^2}{\varepsilon_b^3 d_p^2} u_0 + \frac{1.75 (1 - \varepsilon_b) \rho_g}{\varepsilon_b^3 d_p} |u_0| u_0 \quad 5.2$$

where P is the total pressure, μ_g is the gas viscosity, ρ_g is the gas density and d_p is the particle diameter.

The linear driving force model (LDF) is employed to describe the mass transfer rate in the mesopores/macropores of the material, given by equation 5.3:

$$\frac{\partial \bar{C}_i}{\partial t} = \frac{15 D_{pi}}{R_p^2} (C_{si} - \bar{C}_i) - \frac{\rho_p}{\varepsilon_p} \frac{\partial \bar{q}_i}{\partial t} \quad 5.3$$

where D_{pi} is the pore diffusivity of component i , R_p is the particle radius, ρ_p is the particle density, ε_p is the particle porosity, $\bar{C}_i$ is the average concentration at the mesopores/macropores of component i and $\bar{q}_i$ is the average adsorbed phase concentration of component i .

Mass balance in the micropores is also described using the Linear Driving Force model, expressed by equation 5.4:

$$\frac{\partial \bar{q}_i}{\partial t} = \frac{15 D_{ci}}{R_c^2} (q_i^* - \bar{q}_i) \quad 5.4$$

where D_{ci} is the crystal diffusivity, R_c is the crystal radius, q_i^* is the adsorbed gas phase concentration of component i in equilibrium with $\bar{C}_i$ calculated with the multicomponent Dual-Site Langmuir isotherm.

The fluxes equality at particle surface is given by equation 5.5:

$$\frac{a_p k_f}{\varepsilon_p} (C_{gi} - C_{si}) = \frac{15 D_{pi}}{R_p^2} (C_{si} - \bar{C}_i) \quad 5.5$$

The mathematical model should consider the energy balance for the gas and solid phases and also for the column wall. The gas phase energy balance equation is given by equation 5.6:

$$\begin{aligned} \frac{\partial}{\partial z} \left(\lambda \frac{\partial T_g}{\partial z} \right) - u_0 C_t \tilde{C}_p \frac{\partial T_g}{\partial z} + \varepsilon_b R_g T_g \frac{\partial C_t}{\partial t} - (1 - \varepsilon_b) a_p h_f (T_g - T_p) \\ - \frac{4 h_w}{D_w} (T_g - T_w) - \varepsilon_b C_t \tilde{C}_v \frac{\partial T_g}{\partial t} = 0 \end{aligned} \quad 5.6$$

where $\tilde{C}_v$ and $\tilde{C}_p$ are the gas molar specific heat at constant volume and pressure, respectively, R_g is the ideal gas constant, D_w is the wall internal diameter, λ is the axial heat dispersion coefficient, h_f and h_w are the film heat transfer coefficients between the gas phase and the particle, and the gas phase and the wall. T_g , T_p and T_w are the gas, particle and wall temperatures, respectively,

The energy balance equation to the solid phase is described by equation 5.7:

$$\begin{aligned} (1 - \varepsilon_b) \left[\varepsilon_p \sum_{i=1}^n \bar{C}_{p,i} \tilde{C}_{vi} + \rho_p \sum_{i=1}^n \bar{q}_i \tilde{C}_{v,ads,i} + \rho_p \hat{C}_{p,s} \right] \frac{\partial T_p}{\partial t} = (1 - \varepsilon_b) \left(\varepsilon_p R_g T_p \frac{\partial \bar{C}_t}{\partial t} \right) + \rho_b \left[\sum_{i=1}^n (-\Delta H_i) \frac{\partial \bar{q}_i}{\partial t} \right] + (1 - \varepsilon_b) a_p h_f (T_g - T_p) - \\ \frac{4}{D_w} h_w (T_s - T_w) \end{aligned} \quad 5.7$$

where $\tilde{C}_{v,ads,i}$ is the molar specific heat of component i in the adsorbed phase at constant volume, $\hat{C}_{p,s}$ is the adsorbent specific heat per mass unit and $(-\Delta H_i)$ is the heat of adsorption of component i .

Finally, the energy balance, neglecting the axial heat conduction on the column wall, is described by equation 5.8:

$$\rho_w \tilde{C}_{pw} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_s - T_w) - \alpha_{wl} U (T_w - T_\infty) \quad 5.8$$

where ρ_w is the column wall density, $\tilde{C}_{pw}$ is the column wall specific heat, U is the overall heat transfer coefficient, α_w is the ratio of the internal surface area to the column wall volume and α_{wl} is the ratio of the logarithmic mean surface area of the column shell to the volume of the column wall.

When the adsorbent is regenerated by applying an electric current (Joule effect), the solid energy balance should be adjusted to describe this phenomenon. The term of heat generation by Joule effect should be added to the solid energy balance during electrification step, as described in equation 5.9:

$$\begin{aligned} (1 - \varepsilon_b) \left[\varepsilon_p \sum_{i=1}^n \bar{C}_{pi} \tilde{C}_{vi} + \rho_p \sum_{i=1}^n \bar{q}_i \tilde{C}_{v,ads,i} + \rho_p \tilde{C}_{p,s} \right] \frac{\partial T_p}{\partial t} = (1 - \varepsilon_b) \left(\varepsilon_p R_g T_p \frac{\partial \bar{C}_t}{\partial t} \right) + \rho_b \left[\sum_{i=1}^n (-\Delta H_i) \frac{\partial \bar{q}_i}{\partial t} \right] + (1 - \varepsilon_b) a_p h_f (T_g - T_p) - \\ \frac{4}{d_w} h_w (T_s - T_w) + \frac{VI}{(1 - \varepsilon_b) \pi R_w^2 L} \theta \end{aligned} \quad 5.9$$

where V is the electric potential employed, I is the electric current passing through the resistance and θ is the coefficient of effective energy employed in the adsorbent heating [8].

The ratio of the internal surface area to the column wall volume (α_w) and the ratio of the logarithmic mean surface area of the column shell to the volume of the column wall (α_{wl}) could be determined by equations 5.10 and 5.11:

$$\alpha_w = \frac{D_w}{e(D_w + e)} \quad 5.10$$

$$\alpha_{wl} = \frac{2}{(D_w + e) \ln \left(\frac{D_w + 2e}{D_w} \right)} \quad 5.11$$

where e is the wall thickness.

Some transport parameters that appear in the model equations can be calculated with the following equations.

The pore diffusivity (D_{pi}) can be obtained with the Bosanquet equation (5.12) [9]:

$$\frac{1}{D_{pi}} = \tau_p \left(\frac{1}{D_{mi}} + \frac{1}{D_{ki}} \right) \quad 5.12$$

where D_{mi} is the molecular diffusivity for component i , D_{ki} is the Knudsen diffusivity for component i and τ_p is the particle tortuosity. The molecular diffusivity of the mixture is given by (equation 5.13):

$$D_m = \frac{1 - y_i}{\sum_{j=1, j \neq i}^n \frac{y_j}{D_{ij}}} \quad 5.13$$

where y_i is the molar fraction of component i and D_{ij} is the binary molecular diffusivity, calculated by Chapman-Enskog equation (5.14) [9]:

$$D_{ij} = \frac{2.66 \times 10^{-2} T^{\frac{3}{2}}}{P M_{ij}^{\frac{1}{2}} \sigma_{ij}^2 \Omega_D} \quad 5.14$$

where P and T represent the pressure and temperature of the system, M_{ij} is the molecular weight of the mixture between component i and j , σ_{ij} is the binary constant parameter and Ω_D is the collision integral.

The Knudsen diffusivity can be given by equation 5.15 [9]:

$$D_{ki} = 0.97 r_p \sqrt{\frac{T_g}{M_i}} \quad 5.15$$

where r_p is the pore radius in cm, T_g is the gas temperature and M_i is the molecular weight of component i .

In 1981, Hsu and Haynes developed a correlation to calculate the axial mass and heat dispersions coefficients, valid in a domain of Reynolds values between 0.008 and 50, given by equation 5.16 [10]:

$$D_{ax} = \frac{D_m}{\varepsilon_b} \left(\gamma_1 \varepsilon_b + \gamma_2 \frac{\text{Re Sc}}{1 + 1.8 \gamma_1 \left(\frac{\varepsilon_b}{\text{Re Sc}} \right)} \right) \quad 5.16$$

where Sc and Re are the Schmidt and Reynolds numbers. γ_1 and γ_2 are experimental parameters, equal respectively to $\gamma_1 = 0.75$ and $\gamma_2 = 3.3$.

Besides these equations, the following (equation 5.17 to 5.21) allow determining the Schmidt (Sc), Prandtl (Pr), Nusselt (Nu) and Sherwood (Sh) numbers.

$$Sc = \frac{\mu}{\rho_g D_m} \quad 5.17$$

$$\frac{\lambda}{k_g} = 7 + 0.5 Pr Re \quad 5.18$$

$$Sh = 2.0 + 1.1 Re^{0.6} Sc^{\frac{1}{3}} \quad 5.19$$

$$Nu = 2.0 + 1.1 Re^{0.6} Pr^{\frac{1}{3}} \quad 5.20$$

where k_g is the thermal conductivity of gas.

The properties of the gases, such as, viscosity of the mixture and thermal conductivity were calculated from equations reported in literature [9].

The dual Site Langmuir model was also used to characterize the adsorption in the two different types of adsorption sites, as reported for the extruded honeycomb monolith in Chapter 4. In the multicomponent adsorptive processes, the extension of multicomponent of Dual-Site Langmuir model was used (equation 5.21 and 5.22):

$$q_i = q_{sat,1,i} \frac{b_{1,i} P_i}{1 + \sum_{j=1}^n b_{1,j} P_j} + q_{sat,2,i} \frac{b_{2,i} P_i}{1 + \sum_{j=1}^n b_{2,j} P_j} \quad 5.21$$

$$b_{k,i} = b_{0,k,i} \exp\left(\frac{-\Delta H_{k,i}}{R_g T}\right) \quad 5.22$$

In order to solve the system of partial differential equations, appropriate initial and boundary conditions are needed. In the breakthrough experiments, the initial conditions employed in the simulations were set considering the bed filled with helium (inert gas) or nitrogen at the experiment temperature and pressure. It is also considered that the pressure is controlled at the end of the column. The boundary and the initial conditions used in the mathematical model simulation are shown in Table 5.5.

Table 5.5. Boundary and initial conditions used in mathematical model.

Boundary conditions	
$z = 0, \text{inlet}$	$z = L, \text{outlet}$
$u_{0\text{inlet}}y_{\text{inlet}}C_{\text{inlet},T} = u_0y_{0,i}C_i - \varepsilon_b D_{ax} C_t \frac{\partial y_i}{\partial z}$	$\frac{\partial C_i}{\partial z} = 0$
$u_{0\text{inlet}}C_{\text{inlet},T} = u_0C_T$	$P = P_{\text{outlet}}$
$u_{0\text{inlet}}y_{\text{inlet}}C_{\text{inlet},T}C_pT_{\text{inlet}} = u_0C_TC_pT_g - \lambda \frac{\partial T_g}{\partial z}$	$\frac{\partial T_g}{\partial z} = 0$
Initial conditions	
$y_i = \text{initial composition}$	
$\frac{\partial q}{\partial t} = 0$	
$C_{gT} = C_{gT \text{ inlet}}$	
$T_g = T_s = T_w = T_{\text{inlet}}$	

In order to simulate an ESA cycle, some adjustments should be done in the boundary conditions presented in Table 4.2. In this case, the boundary conditions for the ESA steps employed in the simulations are presented in Table 5.6.

Table 5.6. Boundary conditions used in mathematical model simulation for ESA process.

Boundary conditions	
Feed	
$z = 0, \text{inlet}$	$z = L, \text{outlet}$
$u_{0\text{inlet}}y_{\text{inlet}}C_{\text{inlet},T} = u_0y_{0,i}C_i - \varepsilon_b D_{ax} C_t \frac{\partial y_i}{\partial z}$	$\frac{\partial C_i}{\partial z} = 0$
$u_{0\text{inlet}}C_{\text{inlet},T} = u_0C_T$	$P = P_{\text{feed}}$
$u_{0\text{inlet}}y_{\text{inlet}}C_{\text{inlet},T}C_pT_{\text{inlet}} = u_0C_TC_pT_g - \lambda \frac{\partial T_g}{\partial z}$	$\frac{\partial T_g}{\partial z} = 0$
Closed Column Electrification	
$z = 0$	$z = L$
$\frac{\partial C_i}{\partial z} = 0$	$\frac{\partial C_i}{\partial z} = 0$

$\frac{\partial T_g}{\partial z} = 0$	$\frac{\partial T_g}{\partial z} = 0$
$u_0 = 0$	$u_0 = 0$
Counter-Current Depressurization	
$z = 0, \text{outlet}$	$z = L$
$\frac{\partial C_i}{\partial z} = 0$	$\frac{\partial C_i}{\partial z} = 0$
$\frac{\partial T_g}{\partial z} = 0$	$\frac{\partial T_g}{\partial z} = 0$
$P = P_{high} + (P_{purge} - P_{high}) (1 - \exp(-\beta t))$	$u_0 = 0$
Purge	
$z = 0, \text{outlet}$	$z = L, \text{inlet}$
$\frac{\partial C_i}{\partial z} = 0$	$u_{0inlet} y_{inlet} C_{inlet,T} = u_0 y_{0,i} C_i - \varepsilon_b D_{ax} C_t \frac{\partial y_i}{\partial z}$
$P = P_{purge} + (P_{feed} - P_{purge}) (1 - \exp(-\beta t))$	$u_{0inlet} C_{inlet,T} = u_0 C_T$
$\frac{\partial T_g}{\partial z} = 0$	$u_{0inlet} y_{inlet} C_{inlet,T} C_p T_{inlet} = u_0 C_T C_p T_g - \lambda \frac{\partial T_g}{\partial z}$

The model was implemented in gProms 4.2.0 (PSE Enterprise, United Kingdom) and solved using orthogonal collocation on finite elements method (OCFEM) with second order polynomials over a uniform grid of 100 intervals.

5.4 ADSORPTION EQUILIBRIUM ISOTHERMS

Adsorption equilibrium isotherms of CO₂ and N₂ were determined at three different temperatures, 303, 333, and 373 K in the pressure range of 0 to 1.50 bar, approximately. The measured points, respectively as closed and open for adsorption and desorption results, are presented in Figure 5.15 to Figure 5.18 a) and b). The lines represent the Dual-Site Langmuir model fitting. The isotherm parameters for each compound were determined by the minimization of the sum of the absolute errors between experimental and calculated values from pure adsorption equilibrium isotherms and binary breakthrough experiments with the Excel Solver add-in. The parameters obtained are given in Table 5.7.

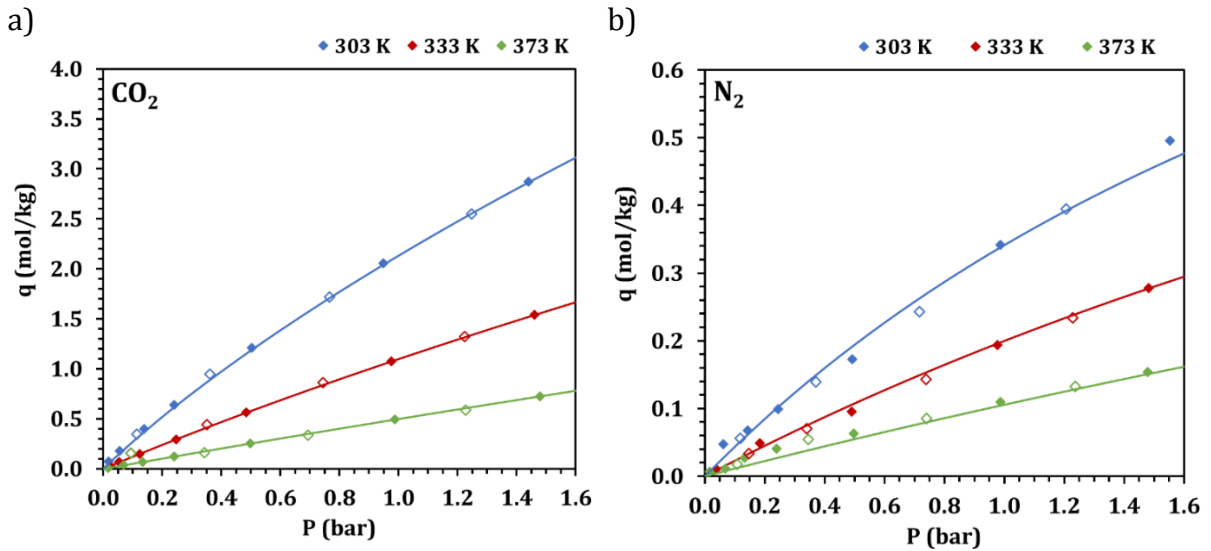


Figure 5.15. Adsorption equilibrium isotherms of a) CO_2 and b) N_2 on 100%AC pellets: experimental points (closed adsorption, open desorption) at 303 K (blue diamonds), 333 K (red diamonds) and 373 K (green diamonds) and Dual-Site Langmuir isotherm fitting (lines).

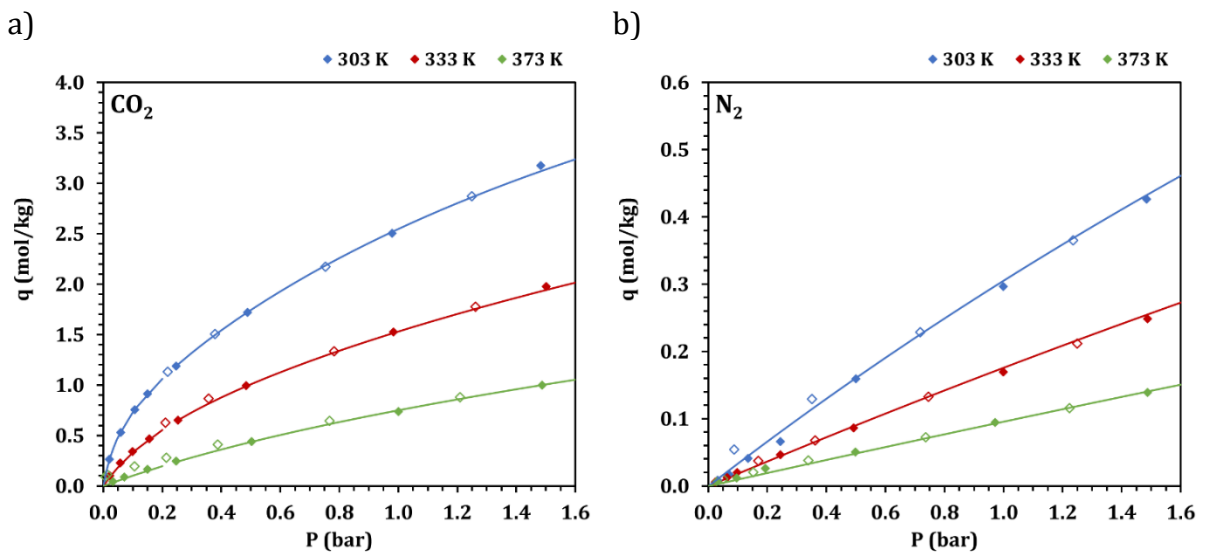


Figure 5.16. Adsorption equilibrium isotherms of a) CO_2 and b) N_2 on 70%AC-30%13X pellets: experimental points (closed adsorption, open desorption) at 303 K (blue diamonds), 333 K (red diamonds) and 373 K (green diamonds) and Dual-Site Langmuir isotherm fitting (lines).

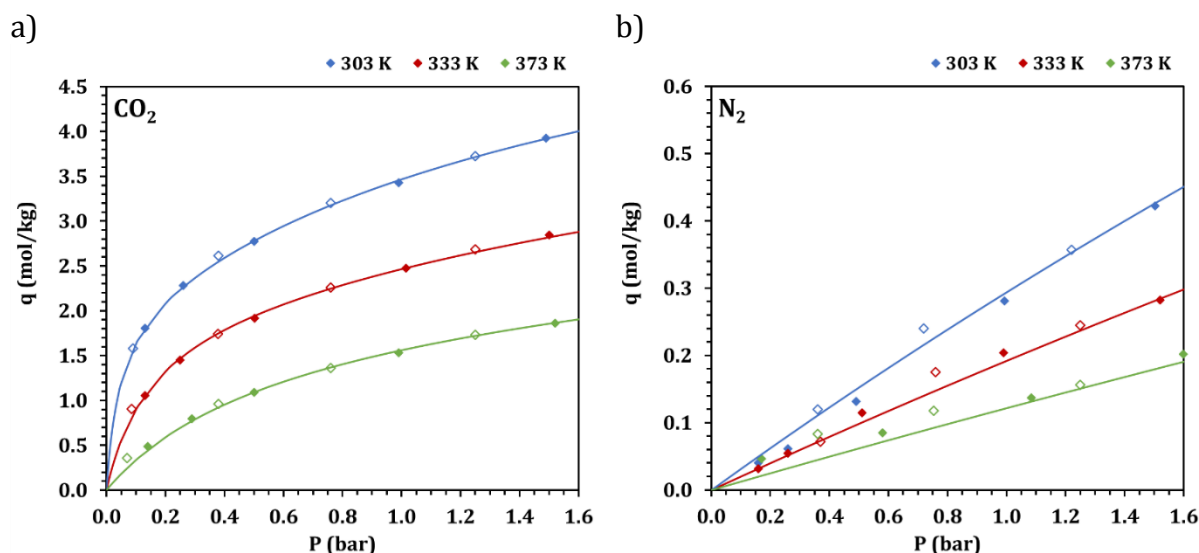


Figure 5.17. Adsorption equilibrium isotherms of a) CO_2 and b) N_2 on 50%AC-50%13X pellets: experimental points (closed adsorption, open desorption) at 303 K (blue diamonds), 333 K (red diamonds) and 373 K (green diamonds) and Dual-Site Langmuir isotherm fitting (lines).

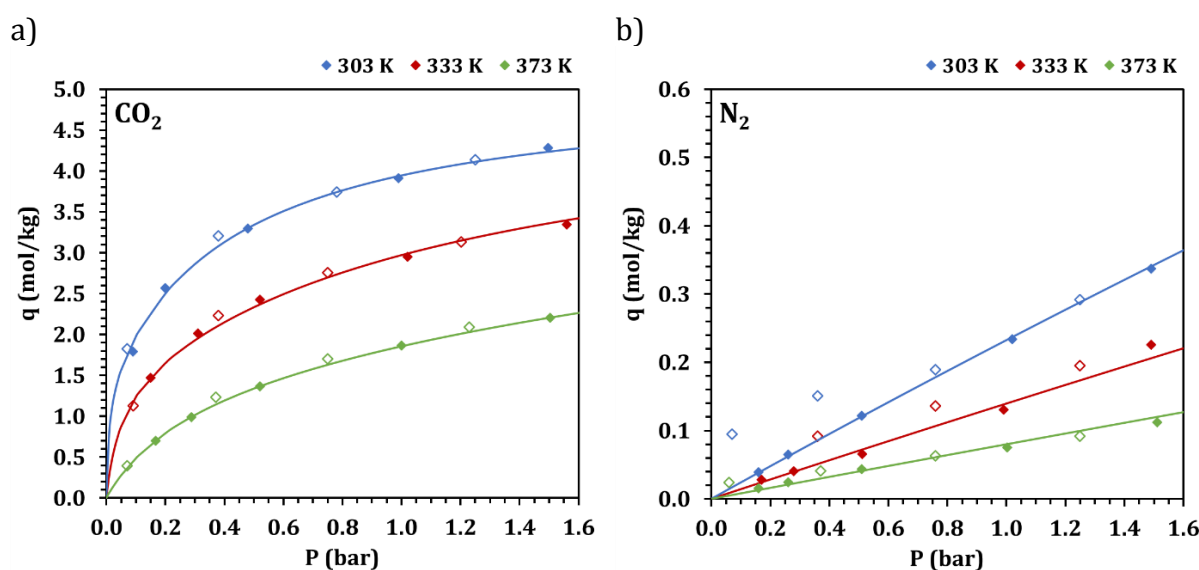


Figure 5.18. Adsorption equilibrium isotherms of a) CO_2 and b) N_2 on 30%AC-70%13X pellets: experimental points (closed adsorption, open desorption) at 303 K (blue diamonds), 333 K (red diamonds) and 373 K (green diamonds) and Dual-Site Langmuir isotherm fitting (lines).

Table 5.7. Fitting parameters for CO₂ and N₂ single component adsorption equilibrium isotherms for the Dual-Site Langmuir model on the different pellets.

Material	$q_{\text{sat},1}$ (mol·kg ⁻¹)	$q_{\text{sat},2}$ (mol·kg ⁻¹)	$b_{0,1}$ (bar ⁻¹)	$b_{0,2}$ (bar ⁻¹)	$(-\Delta H)_1$ (kJ·mol ⁻¹)	$(-\Delta H)_2$ (kJ·mol ⁻¹)
CO₂						
100% AC	13.463	2.322	4.14×10^{-5}	1.37×10^{-5}	19.7	27.1
70%AC- 30%13X	6.489	0.742	2.64×10^{-5}	1.76×10^{-6}	24.2	40.8
50%AC- 50%13X	2.026	4.535	2.95×10^{-5}	6.42×10^{-6}	34.1	28.4
30%AC- 70%13X	3.657	1.415	1.74×10^{-5}	2.55×10^{-6}	29.7	44.1
N₂						
100% AC	0.581	1.406	1.74×10^{-5}	2.09×10^{-4}	7.9	18.5
70%AC- 30%13X	2.379	1.239	3.48×10^{-4}	5.02×10^{-5}	13.1	20.2
50%AC- 50%13X	3.617	0.866	1.86×10^{-4}	3.53×10^{-3}	14.5	8.9
30%AC- 70%13X	3.684	0.100	1.83×10^{-4}	1.00×10^{-6}	10.0	14.9

Observing all figures, in general a good fitting was obtained for the two gases measured in the whole range of pressure and temperature studied. As expected, CO₂ is the most adsorbed component, when compared with N₂. In addition, it was possible to verify the increase of CO₂ adsorbed in line with the increase of amount of zeolite in the sample. The opposite occurs with N₂, because the affinity of this gas in zeolite 13X is less than in activated carbon, therefore the nitrogen adsorbed in the 100%AC sample is higher than in the others. The steeper increase of quantity adsorbed of CO₂ at low pressures, characteristic behaviour of the zeolite 13X, is more remarked in the samples with higher zeolite quantity.

For a better comparison between the different pellets produced, Figure 5.19 a) and b) gives the CO₂ and N₂ adsorption isotherms of all pellets at 303 K, respectively.

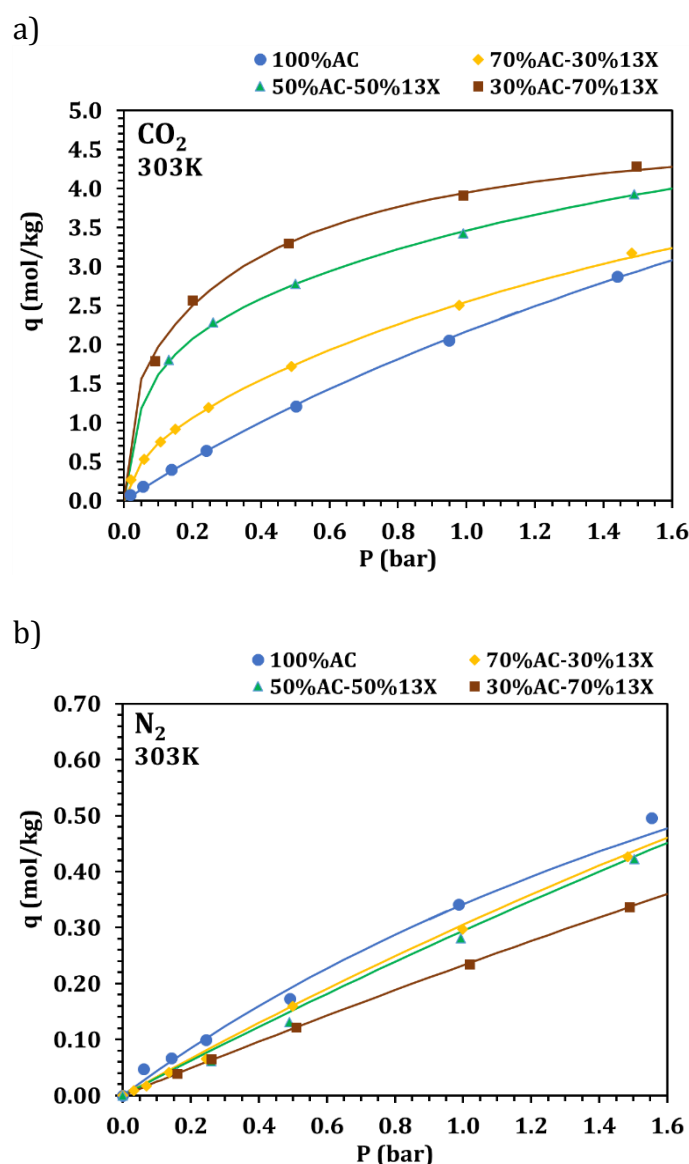


Figure 5.19. Adsorption equilibrium isotherms of a) CO₂ and b) N₂ on 100%AC (blue circles), 70%AC-30%13X pellets (yellow diamonds), 50%AC-50%13X (green triangles) and 30%AC-70%13X (brown squares) at 303 K: experimental points (closed adsorption) and Dual-Site Langmuir isotherm fitting (lines).

The CO₂/N₂ selectivity of pellets has the following order: 30%AC-70%13X > 50%AC-50%13X > 70%AC-30%13X > 100%AC. Values of 62.8, 41.9, 24.6, 12.2 are obtained respectively, considering multicomponent adsorption of a 20%/80% CO₂/N₂ mixture at 1.50 bar and 298 K. Then, in terms of adsorption capacity, 30%AC-70%13X pellets are the best option.

5.4.1 ISOSTERIC HEATS OF ADSORPTION

From the adsorption equilibrium data, isosteric heats of adsorption as function of the loading of each gas adsorbed can be determined. Clausius-Clapeyron equation (equation 3.20 of section 3.7.3 of Chapter 3) was employed. Figure 5.20 and Figure 5.21 present the values calculated for CO₂ and N₂ and show the heats of adsorption obtained through the Dual-Site Langmuir model (equation 5.21) fitting.

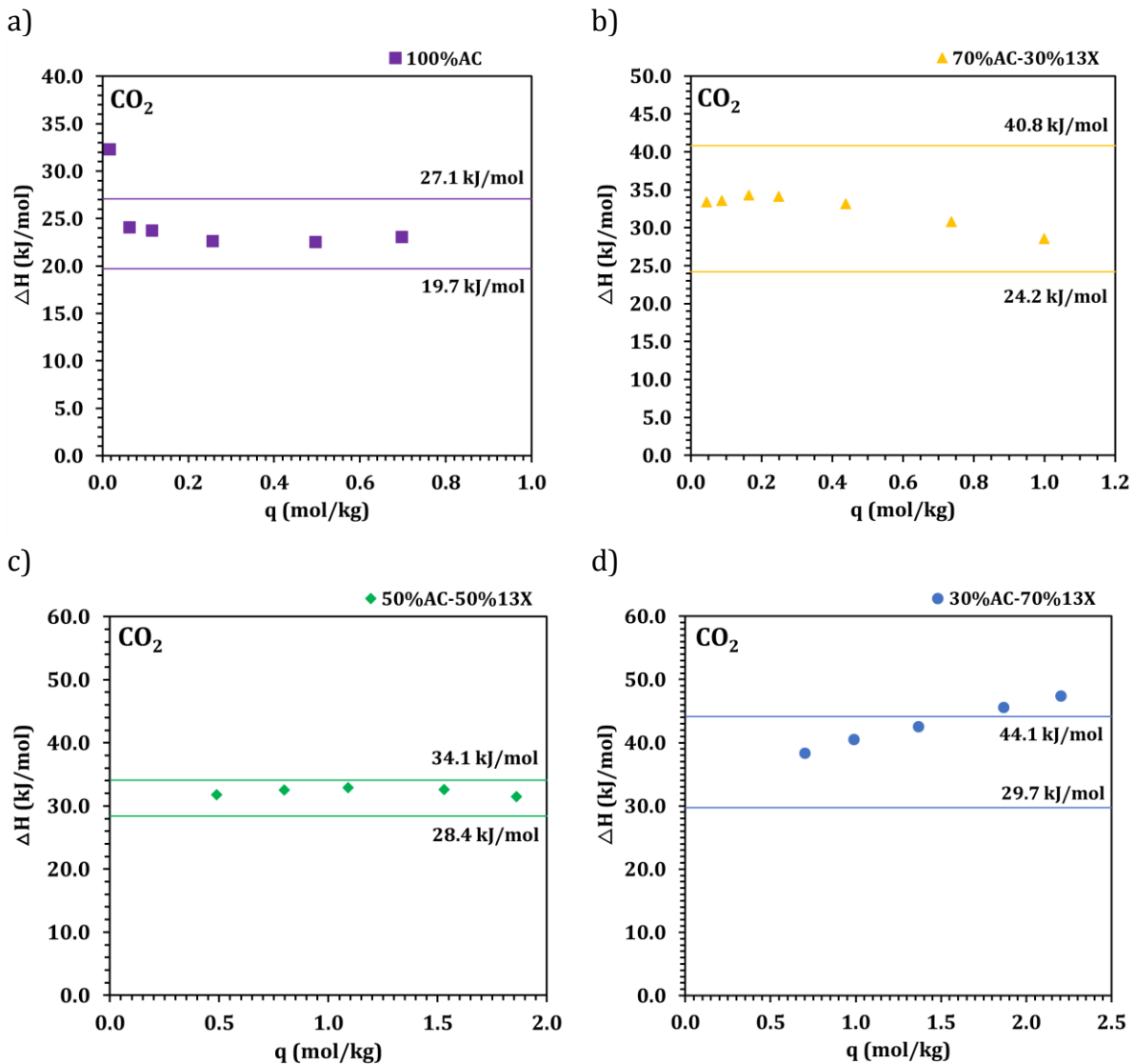


Figure 5.20. Isosteric heats of adsorption of CO₂ for 100%AC (purple squares) pellets, 70%AC-30%13X pellets (yellow triangles), 50%AC-50%13X pellets (green diamonds) and 30%AC-70%13X pellets (blue circles). Points represent the values calculated from adsorption equilibrium data. Horizontal lines represent the values obtained from Dual-Site Langmuir model fitting.

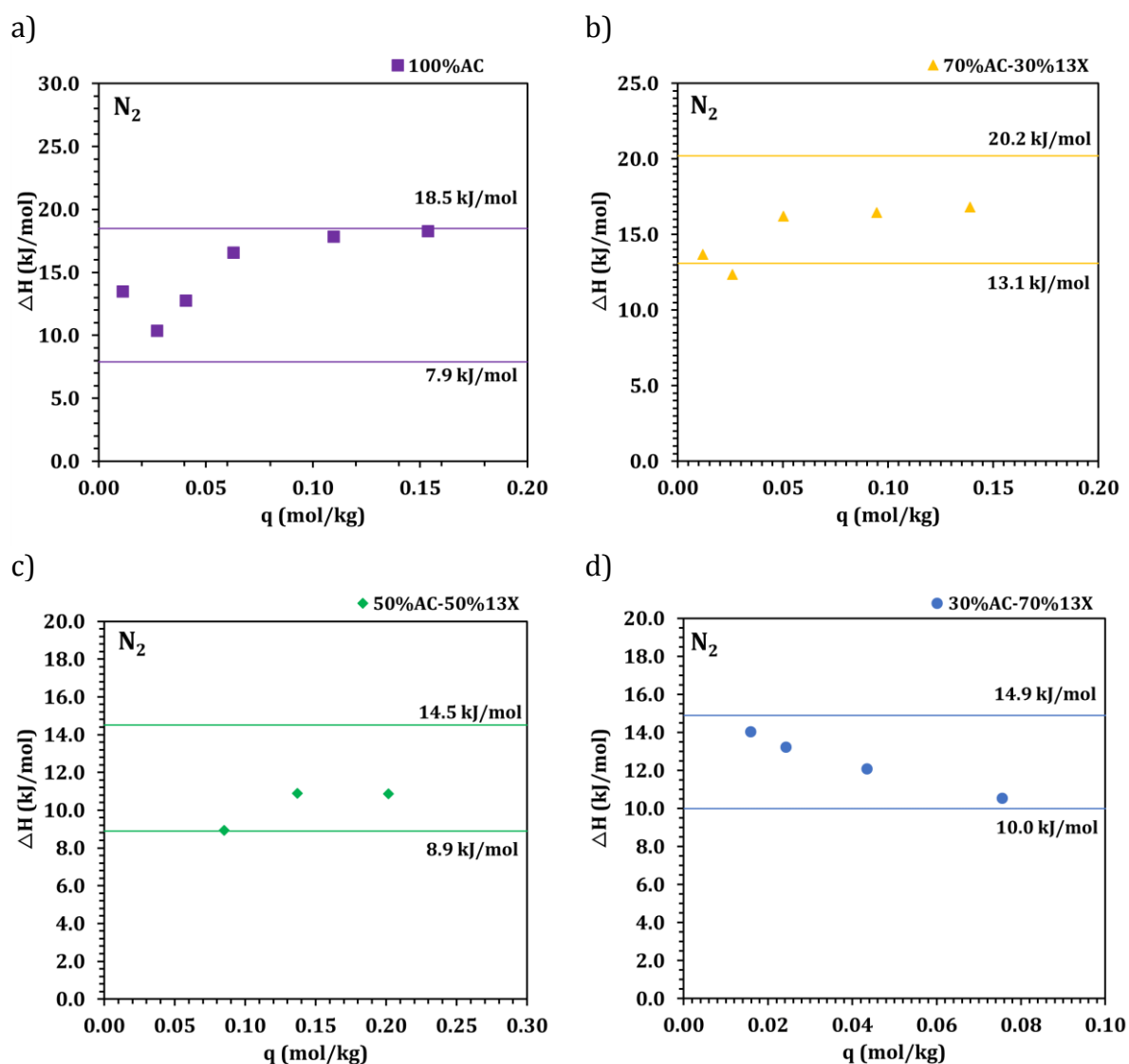


Figure 5.21. Isosteric heats of adsorption of N_2 for 100%AC (purple squares) pellets, 70%AC-30%13X pellets (yellow triangles), 50%AC-50%13X pellets (green diamonds) and 30%AC-70%13X pellets (blue circles). Points represent the values calculated from adsorption equilibrium data. Horizontal lines represent the values obtained from Dual-Site Langmuir model fitting.

Figure 5.20 and Figure 5.21 show the isosteric heat of adsorption obtained for CO_2 and N_2 as a function of the amount adsorbed and the heats of adsorption obtained in the multicomponent Dual-Site Langmuir model fitting. The latter values do not change with loading according to the assumption of adsorbent homogeneous surface. In general, the isosteric heat of adsorption calculated from the experimental data and the values estimated from Dual-Site model demonstrated a good agreement, i.e., in each case, it was possible to observe that all experimental points were located within or very close to the range of the isosteric heats for each site.

According to the multicomponent fitting parameters, the heat of adsorption of CO₂ is higher than N₂.

5.5 BREAKTHROUGH CURVE EXPERIMENTS

5.5.1 EXPERIMENTAL CONDITIONS

To determine the adsorption kinetics of pure gases and mixtures, breakthrough curves were carried out in a lab-scale fixed-bed unit, as described in section 3.8 of Chapter 3. A new column design was developed to pack the pellets and to conduct electric current, in an isolated form and without gas leaks. For these experiments, a stainless-steel column with internal cylindrical shape with a diameter of 3 cm and 10 cm of length was designed. A scheme of the new column is presented in Figure 5.22.

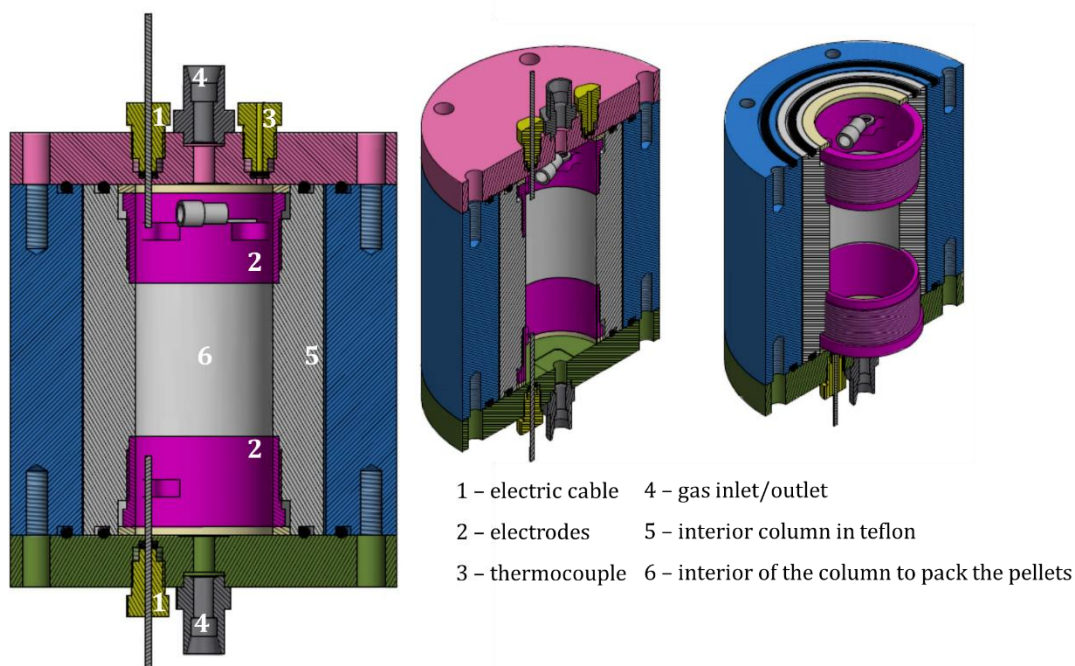


Figure 5.22. New column designed for breakthrough curve and electrification experiments performed with the pellets.

The column is composed by two parts: an external stainless-steel jacket and an internal teflon column. The adsorbent is placed inside the teflon column (6) where two aluminium electrodes are placed, one at the top and another at the base of the column. The thermocouple is inserted in the top of column (3) and it is placed in the middle of the bed in order to measure the temperature history of the pellets. The gas inlet/outlet (4) connections are done with two Swagelok connections.

Single and binary breakthrough curves were carried out in accordance with the experimental conditions given in Table 5.8 after sample activation. The activation conditions, dimensions of the packed bed and the final dry mass of adsorbent for each type of pellets are shown in Table 5.8. The operating conditions of all experiments performed, single and binary, are presented in Table 5.9 to Table 5.12.

Table 5.8. Experimental conditions used in the breakthrough curve experiments performed with the pellets.

Parameter	100%AC	70%AC- 30%13X	50%AC- 50%13X	30%AC- 70%13X
Bed diameter (m)		0.030		
Bed length (m)		0.06		
Dry m_{ads} (g)	9.33	8.92	10.64	14.79
Bulk density ($kg \cdot m^{-3}$)	220	210	251	330
Bed porosity	0.40	0.39	0.41	0.40

Table 5.9. Operating conditions employed in the breakthrough curve experiments performed with the 100%AC pellets (Ads, Des and Elec are an abbreviation for adsorption, desorption and electrification, respectively).

Experiment	Exp.1	Exp.2	Exp.3	Exp.4	Exp.5	Exp.6
Temperature (K)	297.7	297.7	297.0	298.15	298.5	298.5
Pressure (bar)	1.39	1.39	1.37	1.39	1.26	1.32
Flow rate ^a (SLPM)	0.196	0.200	0.196 0.190	0.196	0.200 0.206	0.193
Starting Des (s)	-	2000	2000	-	2000	2000
Elec period (s)	110 - 1010	-	2000 - 3000	65-650	-	2000- 2315

Constant voltage (V)	16	-	16	16	-	16
Desorption gas	-	He	He	-	N ₂	N ₂
Column initial condition ^b	He	He	He	N ₂	N ₂	N ₂
Feed molar fraction	CO ₂ :0 He:1	CO ₂ :0.222 He:0.778	CO ₂ :0.214 He:0.786	CO ₂ :0 N ₂ :1	CO ₂ :0.230 N ₂ :0.760	CO ₂ :0.221 N ₂ :0.779

^aFlow rate of adsorption (with feed) and desorption (with He or N₂) steps, respectively.
^bAt the beginning of the experiment, the column was saturated with He or N₂.

Table 5.10. Operating conditions employed in the breakthrough curve experiments performed with the 70%AC-30%13X pellets (Ads, Des and Elec are an abbreviation for adsorption, desorption and electrification, respectively).

Experiment	Exp.1	Exp.2	Exp.3	Exp.4	Exp.5	Exp.6
Temperature (K)	299.0	296.5	297.6	298.0	296.3	297.65
Pressure (bar)	1.39	1.39	1.44	1.30	1.23	1.32
Flow rate ^a (SLPM)	0.185	0.186	0.190	0.181	0.214 0.225	0.175 0.187
Starting Des (s)	-	2000	2000	-	2000	2000
Elec period (s)	100- 1000	-	2000- 3000	300-800	-	2000- 3000
Constant voltage (V)	18	-	18	18	-	18
Desorption gas	-	He	He	-	N ₂	N ₂
Column initial conditions. ^b	He	He	He	N ₂	N ₂	N ₂
Feed molar fraction	CO ₂ :0 He:1	CO ₂ :0.204 He:0.796	CO ₂ :0.259 He:0.741	CO ₂ :0 N ₂ :1	CO ₂ :0.233 N ₂ :0.767	CO ₂ :0.231 N ₂ :0.769

^aFlow rate of adsorption (with feed) and desorption (with He or N₂) steps, respectively.
^bAt the beginning of the experiment, the column was saturated with He or N₂.

Table 5.11. Operating conditions employed in the breakthrough curve experiments performed with the 50%AC-50%13X pellets (Ads, Des and Elec are an abbreviation for adsorption, desorption and electrification, respectively).

Experiment	Exp.1	Exp.2	Exp.3	Exp.4	Exp.5	Exp.6
Temperature (K)	298.3	298.0	298.9	298.15	297.0	300.6
Pressure (bar)	1.30	1.30	1.50	1.30	1.32	1.32
Flow rate ^a (SLPM)	0.210	0.214 0.200	0.186 0.162	0.200	0.194 0.205	0.201 0.210
Starting Des (s)	-	3000	3000	-	2500	2000
Elec period (s)	200-1100	-	3000- 4150	230-930	-	2000- 2800
Constant voltage (V)	18	-	18	18	-	18
Desorption gas	-	He	He	-	N ₂	N ₂
Column initial conditions ^b	He	He	He	N ₂	N ₂	N ₂
Feed molar fraction	CO ₂ :0 He:1	CO ₂ :0.200 He:0.800	CO ₂ :0.255 He:0.745	CO ₂ :0 N ₂ :1	CO ₂ :0.232 N ₂ :0.768	CO ₂ :0.235 N ₂ :0.765

^aFlow rate of adsorption (with feed) and desorption (with He or N₂) steps, respectively.

^bAt the beginning of the experiment, the column was saturated with He or N₂.

Table 5.12. Operating conditions employed in the breakthrough curve experiments performed with the 30%AC-70%13X pellets (Ads, Des and Elec are an abbreviation for adsorption, desorption and electrification, respectively).

Experiment	Exp.1	Exp.2	Exp.3
Temperature (K)	299.0	298.5	299.6
Pressure (bar)	1.32	1.32	1.35
Flow rate ^a (SLPM)	0.194	0.216 0.211	0.190 0.199
Starting Des (s)	-	3000	3000

Elec period (s)	50-1050	-	-
Constant voltage (V)	18	-	-
Desorption gas	-	He	He
Column initial cond. ^b	He	He	He
Feed molar fraction	CO ₂ :0 He:1	CO ₂ :0.210 He:0.790	CO ₂ :0.225 He:0.775

^aFlow rate of adsorption (with feed) and desorption (with He or N₂) steps, respectively.

^bAt the beginning of the experiment, the column was saturated with He or N₂.

Before each experiment, the column was fed with helium or nitrogen at the feed temperature and pressure. During the feed step, the gas mixture was fed to the column until saturation. Then, in the desorption step, helium or nitrogen was fed to the column. Each breakthrough curve was simulated, and the experimental data were compared with simulations results.

The following sections (5.5.2 to 5.5.5) present the results for each type of pellets. The Figures in each section report the results of molar fraction history of each component at the column outlet (graphic a), total flow rate at the column outlet (graphic b), temperature history at 0.03 m (graphic c). In these graphics, the experimental data are represented by points and the simulations results by lines. The transport parameters values required for the simulations were calculated at feed conditions using the correlations presented in mathematical model section (5.3). These were kept constant during the simulations.

In the case of experiments in which the feed composition was not changed (heating experiments only – Exp. 1 and Exp. 4), the results show only the temperature history at 0.03 m.

5.5.2 100%AC PELLETS

In experiment 1, the pellets were electrified between 110 s (power on) and 1010 s (power off) in order to increase the temperature of the solid by Joule effect, while a stream of helium was being fed to the column. Figure 5.23 shows the results obtained.

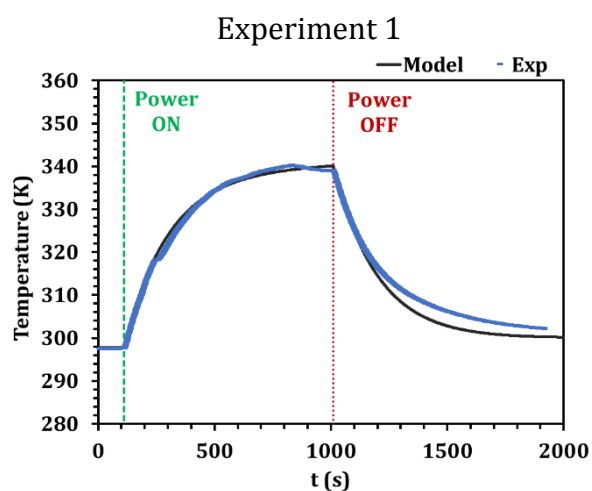
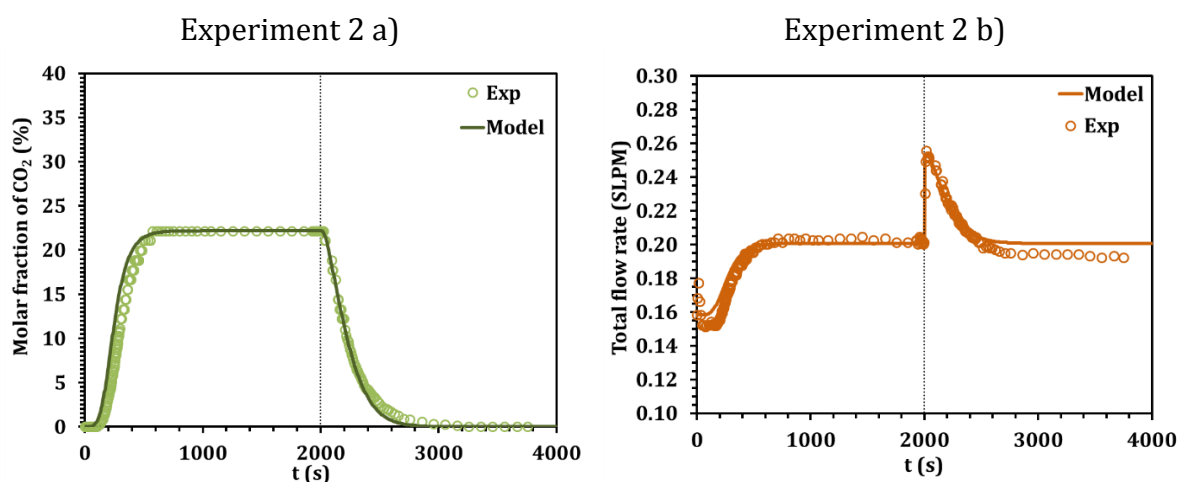


Figure 5.23. Results of experiment 1 with 100%AC pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

As observed in Figure 5.23, the temperature of the pellets increased until 340 K in a period of 900 s, approximately. The model fitted the experimental data with high accuracy during heating, and a slightly difference in the temperature decrease was verified.

In experiment 2, a single breakthrough curve with carbon dioxide in helium was carried out. The results are given in Figure 5.24.



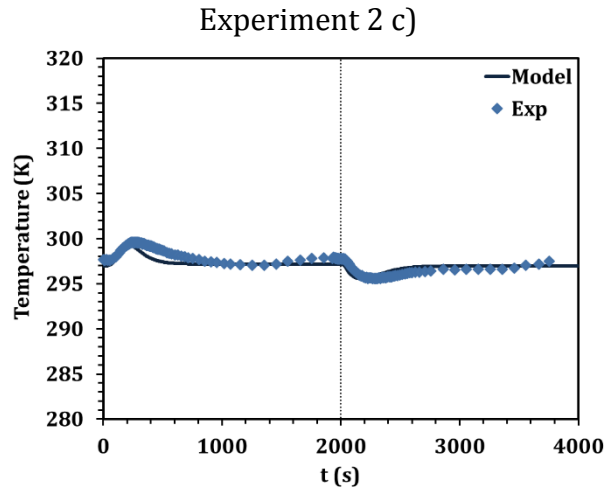
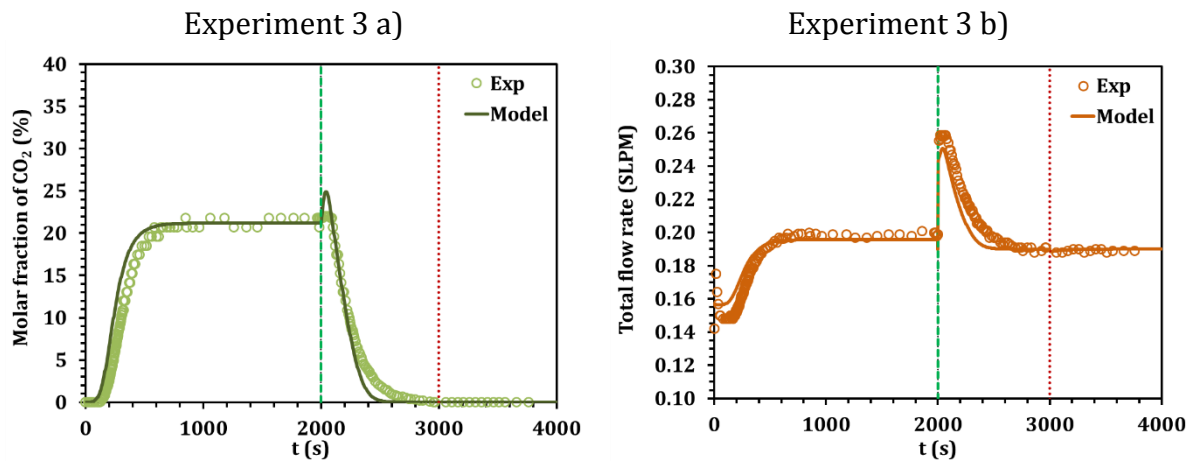


Figure 5.24. Breakthrough curve results of experiment 2 with 100%AC pellets for inlet total pressure of 1.39 bar at 298 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

The same single breakthrough curve with carbon dioxide was done with electrification of the pellets during 1000 s in the desorption step. The results of this experiment 3 can be observed in Figure 5.25.



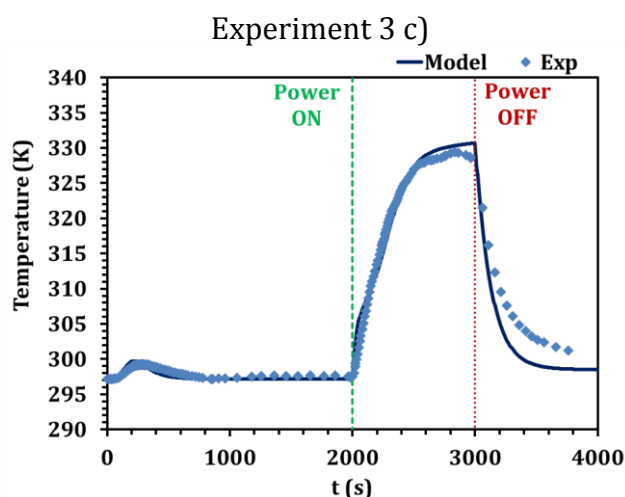


Figure 5.25. Breakthrough curve results of experiment 3 with 100%AC pellets for inlet total pressure of 1.37 bar at 297 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

Experiments 2 and 3 were carried out in order to understand the influence of the temperature on the CO₂ desorption. As observed, in the breakthrough experiment without electrification, the molar fraction of CO₂ reached 0% at 3200 s, approximately, while in experiment 3, increasing temperature until 330 K by electrification, the regeneration was completed at 2950 s, approximately.

In experiment 4, an electric current was applied in the adsorbent material between 65 s and 650 s in order to increase temperature, but in this case a stream of nitrogen was being fed to the column (Figure 5.26).

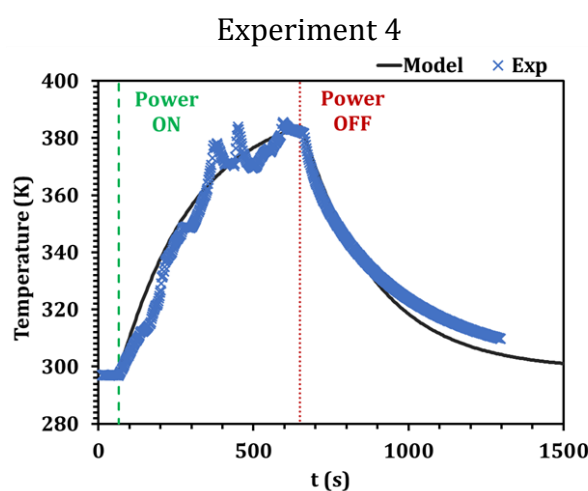


Figure 5.26. Results of experiment 4 with 100%AC pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

In a nitrogen environment, the 100%AC pellets reached 380 K in 600 s, approximately.

Experiment 5 was carried out using a binary stream with carbon dioxide and nitrogen. The results are given in Figure 5.27.

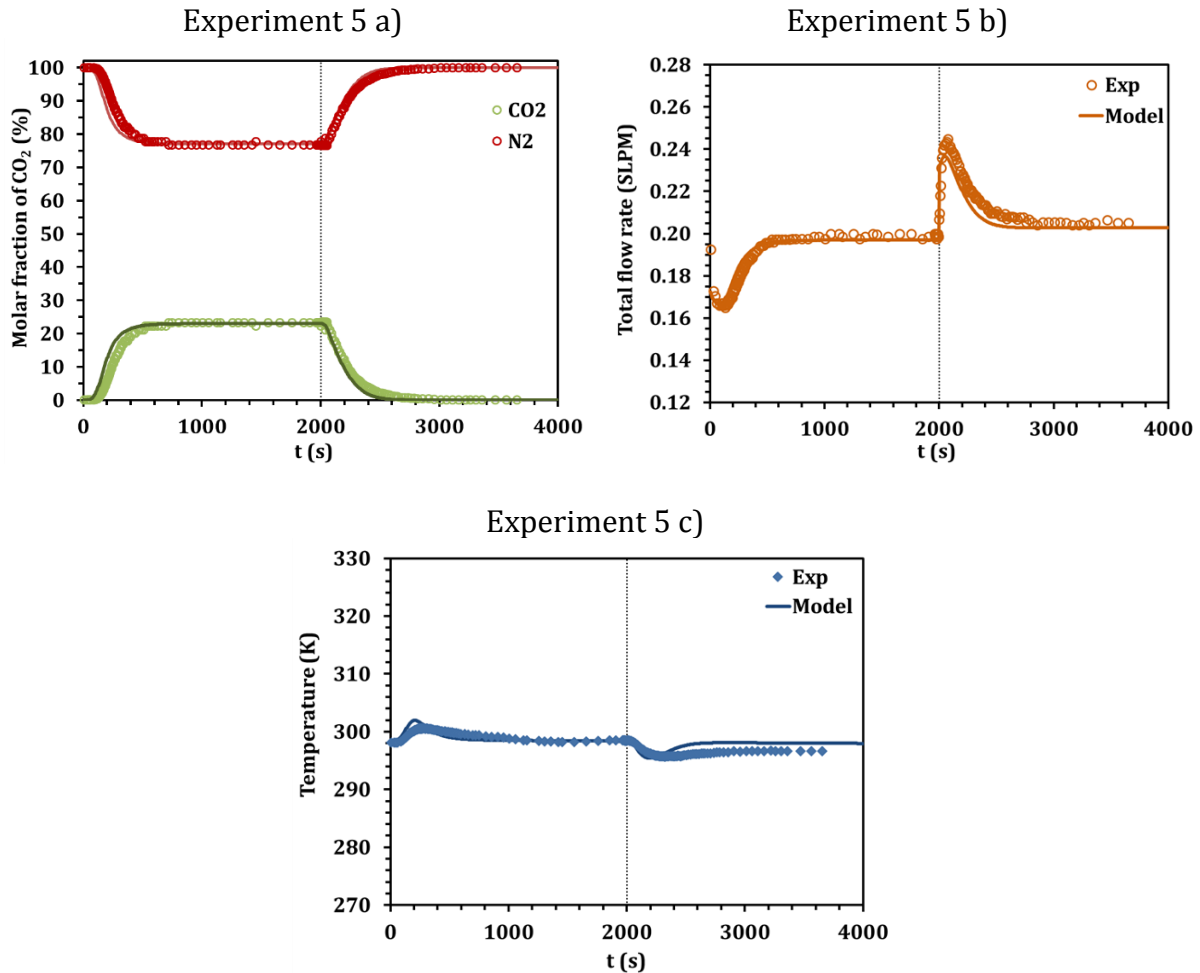


Figure 5.27. Breakthrough curve results of experiment 5 with 100%AC pellets for inlet total pressure of 1.26 bar at 298.5 K: CO_2 molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

It is possible to observe in Figure 5.27 that the adsorbent is regenerated after 3100 s, approximately.

Experiment 6 presents the results of the binary CO_2/N_2 breakthrough experiment with electrification in the desorption step. In this experiment, the electrification was performed between 2000 s and 2315 s.

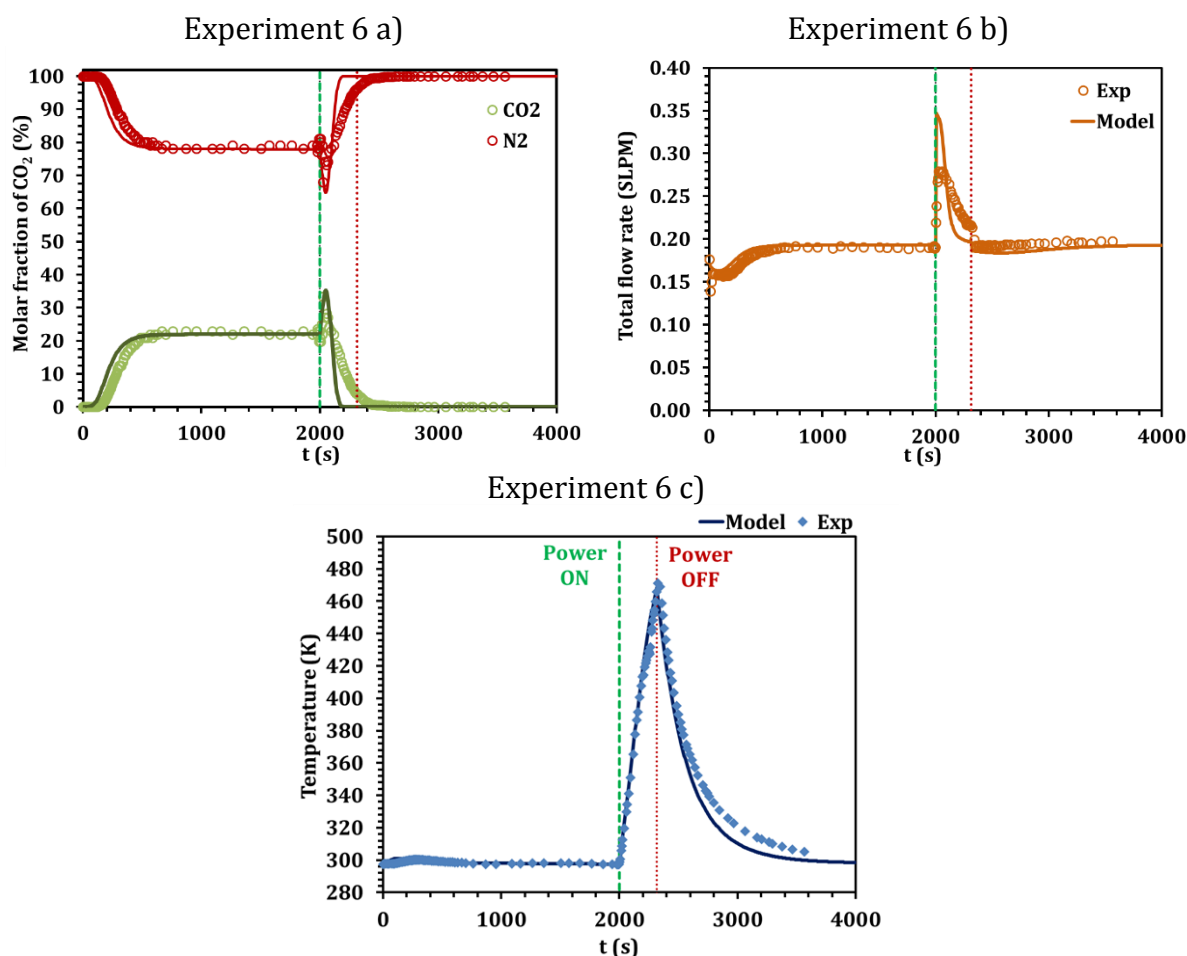


Figure 5.28. Breakthrough curve results of experiment 6 with 100%AC pellets for inlet total pressure of 1.32 bar at 298.5 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

Comparing the two binary breakthrough experiments (experiment 5 and 6), it was observed that in experiment 6, the molar fraction of CO₂ reached 0% at 2730 s (less 400 s).

In general, the results obtained for the 100%AC pellets demonstrated a good agreement between the experimental data and the simulations results. In each breakthrough curve, first, it is possible to observe an increase in the flow rate and CO₂ molar fraction as this component reached the bed outlet, representing the adsorption step. Then, it was observed an increase of flow rate due to the release of the adsorbed gas and afterward the flow starts to decrease, representing the desorption step. The temperature history presents the expected increase and decrease during adsorption and desorption. However, as 100%AC pellets have poor CO₂ adsorption capacity, this

temperature variation is very small. In binary breakthrough curve, the multicomponent Dual-Site Langmuir model was considered, and the experimental results are well predicted.

In the simulations, the heat transfer parameters h_w and U were fitted. It was observed that these parameters have low values, due to the low heat transfer that occurs because of the interior teflon column. Table 5.13 reports the values of the transport parameters used in the simulations as well as the values of the electric current intensities.

Table 5.13. Transport parameters values used in the simulations of the breakthrough experiments with the 100%AC pellets.

Experiment	Exp.1 He Heat	Exp.2 CO ₂ /He	Exp.3 CO ₂ /He Heat	Exp.4 N ₂ Heat	Exp.5 CO ₂ /N ₂	Exp.6 CO ₂ /N ₂ Heat
$D_{p,i} \times 10^6$ (m ² ·s ⁻¹)	2.00	CO ₂ : 0.61 He: 1.90	CO ₂ : 0.61 He: 1.90	2.00	CO ₂ : 5.70 N ₂ : 0.70	CO ₂ : 5.70 N ₂ : 0.70
$D_{c,i} \times 10^7$ (m ² ·s ⁻¹)	-	CO ₂ : 5.76	CO ₂ : 5.76	3.90	CO ₂ : 5.76 N ₂ : 21.45	CO ₂ : 5.76 N ₂ : 21.45
$D_{ax} \times 10^5$ (m ² ·s ⁻¹)	8.9	5.2	5.1	8.8	5.7	5.7
k_f (m·s ⁻¹)	0.11	0.047	0.045	0.12	0.016	0.016
h_f (W·m ⁻² ·K ⁻¹)	146	90	92.8	29.5	27.6	27.6
h_w (W·m ⁻² ·K ⁻¹)	3.5	35	5	1.75	15	5
U (W·m ⁻² ·K ⁻¹)	7	5	5	5	5	25
I (A)	0.06	-	0.07	0.09	-	0.28

5.5.3 70%AC-30%13X PELLETS

The results of the experiments performed with the 70%AC-30%13X pellets are presented in the following Figure 5.29 to Figure 5.36, for experiment 1 to experiment 6.

In experiment 1, the pellets were submitted to an electric current between 100 s (power on) and 1000 s (power off) while a stream of helium was being fed to the column, in order to increase the temperature of the solid by Joule effect. Figure 5.29 shows the results of this experiment.

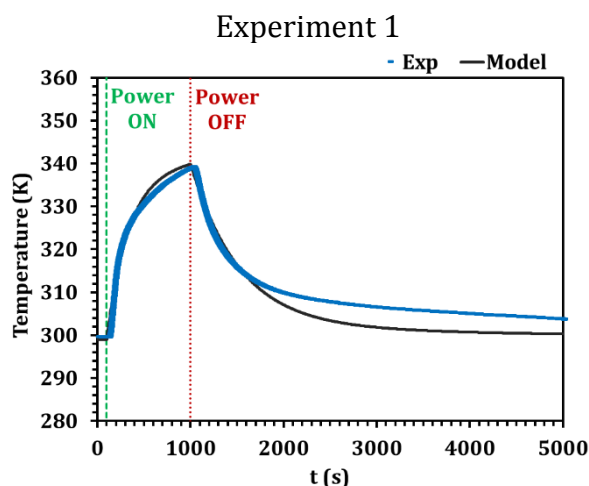
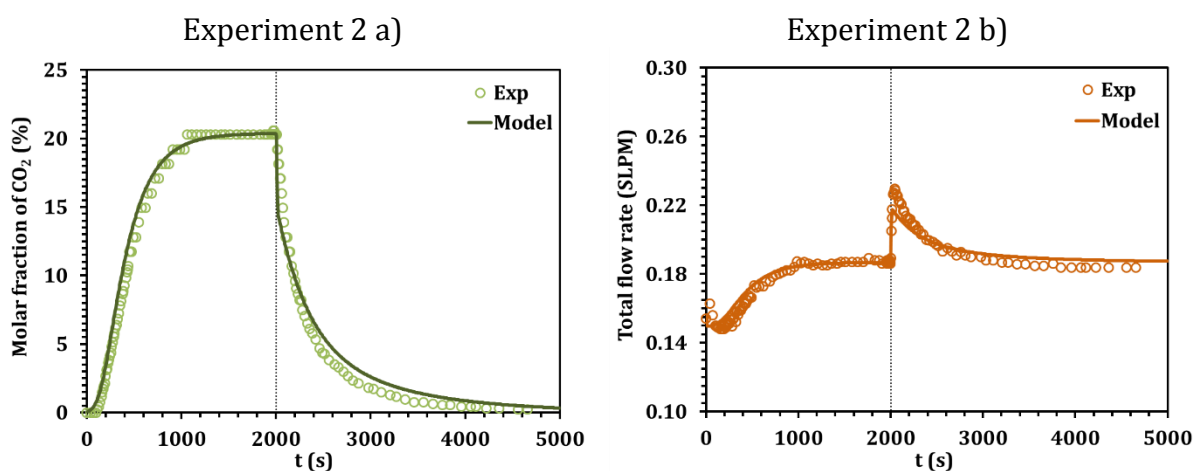


Figure 5.29. Results of experiment 1 with 70%AC-30%13X pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

As observed in Figure 5.29, the measured temperature increased until 338 K in a period of 900 s, approximately.

In experiment 2, a single breakthrough curve with carbon dioxide was carried out and the results of this experiment are given in Figure 5.30.



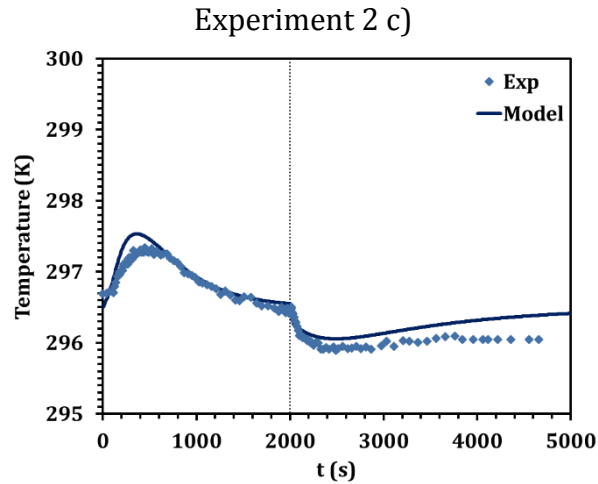
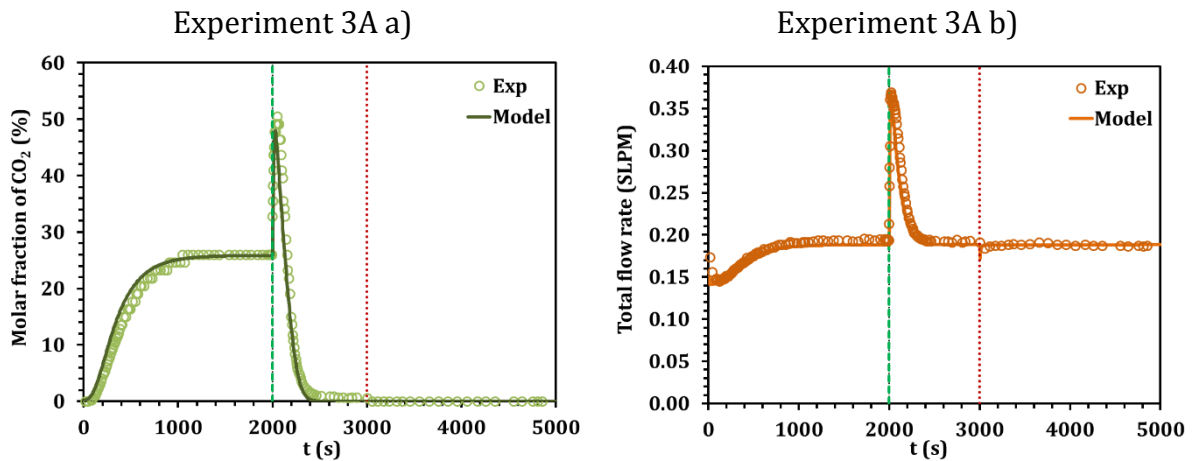


Figure 5.30. Breakthrough curve results of experiment 2 with 70%AC-30%13X pellets for inlet total pressure of 1.39 bar at 296.5 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

In experiment 3, a single breakthrough curve with carbon dioxide and electrification of the pellets during desorption step was performed. Two simulations of the experimental data are presented, Figure 5.31 and Figure 5.32.



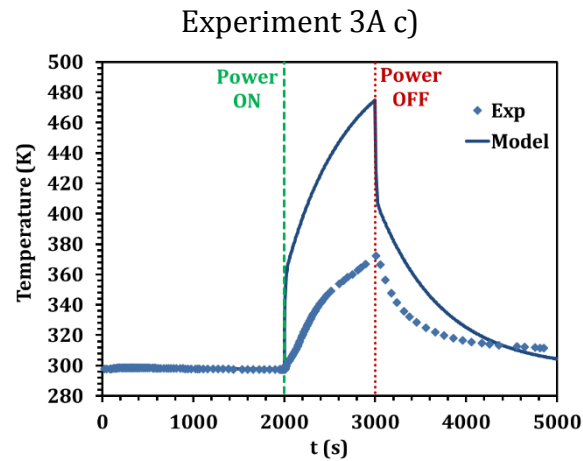
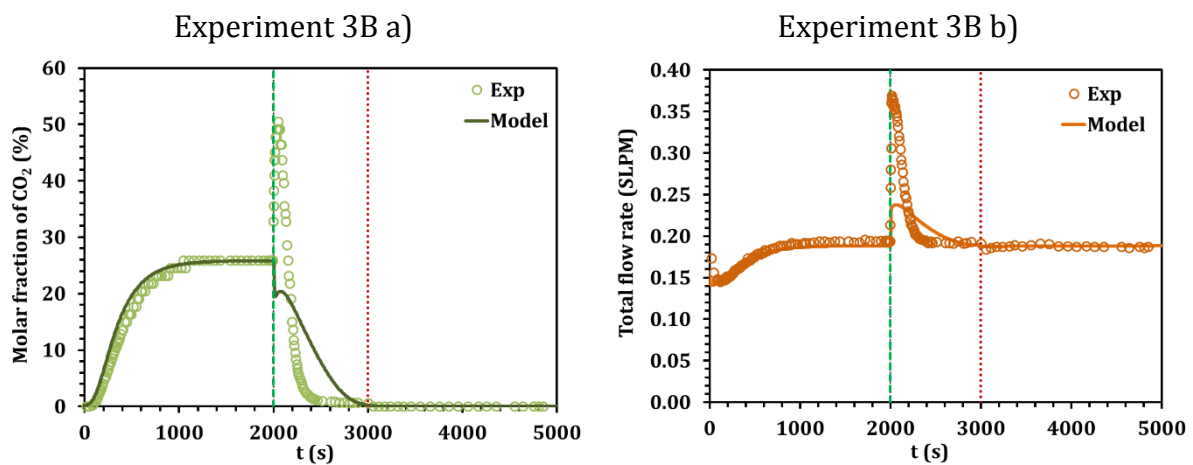


Figure 5.31. Breakthrough curve results of experiment 3 with 70%AC-30%13X pellets for inlet total pressure of 1.44 bar at 298 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

In terms of molar fraction and total flow rate, Figure 5.31 shows an excellent agreement with the experimental data. The model was able to predict the increase of molar fraction when the desorption step starts. However, analysing the temperature, a large difference between the experimental data and the simulated results are observed, because the model predicts that temperature should reach a value of 480 K, but experimentally, only an increase until 370 K was observed. Figure 5.32 shows the same experimental data but with a new simulation, with different heat transfer parameters in order to predict the experimental temperature observed.



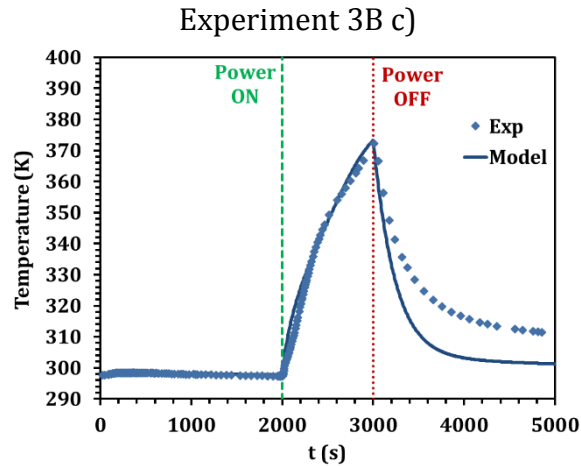


Figure 5.32. Breakthrough curve results of experiment 3 with 70%AC-30%13X pellets for inlet total pressure of 1.44 bar at 298 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

In this case, the simulation shows a poor prediction of the molar fraction and total flow rate at the column outlet, contrarily to the previous simulation.

Comparing experiment 2 and experiment 3, it was observed that the molar fraction of CO₂ reached 0% at 4500 s, approximately, while in the experiment 3 the regeneration was completed at 3000 s, approximately.

In experiment 4, an electric current was applied at the adsorbent material in order to increase temperature when the nitrogen was fed to the column, between 300 s and 800 s.

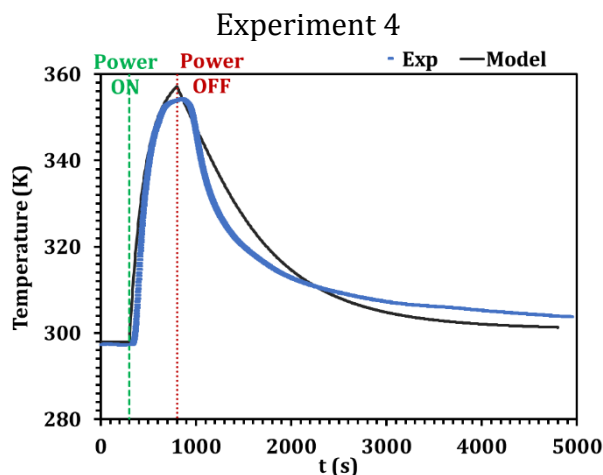


Figure 5.33. Results of experiment 4 with 70%AC-30%13X pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

In an ambient with nitrogen, thermocouple reading reached 350 K in 500 s, approximately, i.e., high temperature in less time when compared with the experiment 1.

The experiment 5 was performed using a feed stream with a binary mixture of carbon dioxide and nitrogen. The results are given in Figure 5.34.

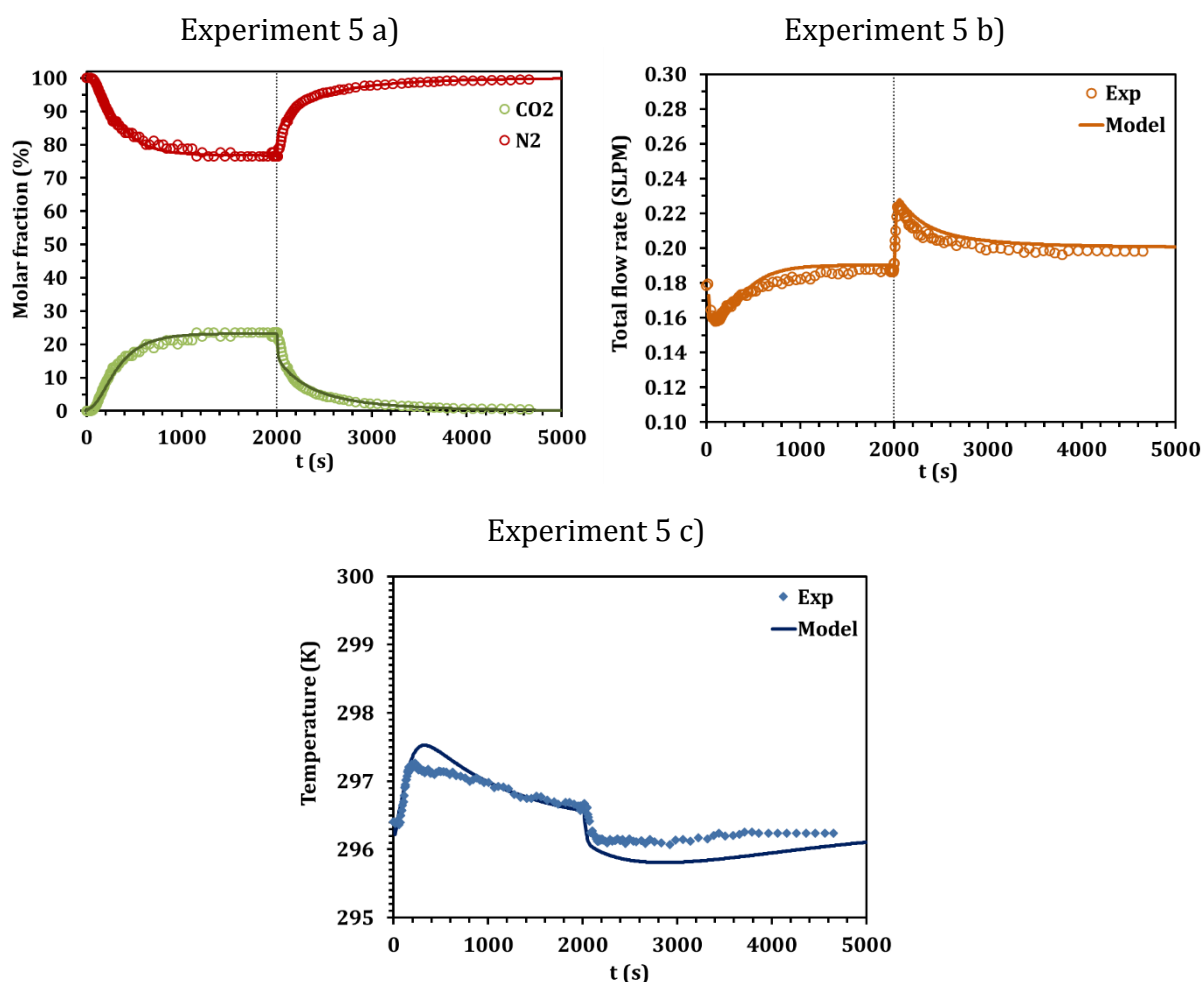


Figure 5.34. Breakthrough curve results of experiment 5 with 70%AC-30%13X pellets for inlet total pressure of 1.23 bar at 296 K: CO_2 molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

In experiment 5, the adsorbent was regenerated after 4500 s, approximately. In terms of temperature, a small increase of about 1.5 K was verified due to the adsorption phenomenon.

Figure 5.35 shows the results of the experiment 6, which corresponds to a binary CO_2/N_2 breakthrough curve with electrification in the desorption step. In this experiment, the electrification was performed between 2000 s and 3000 s.

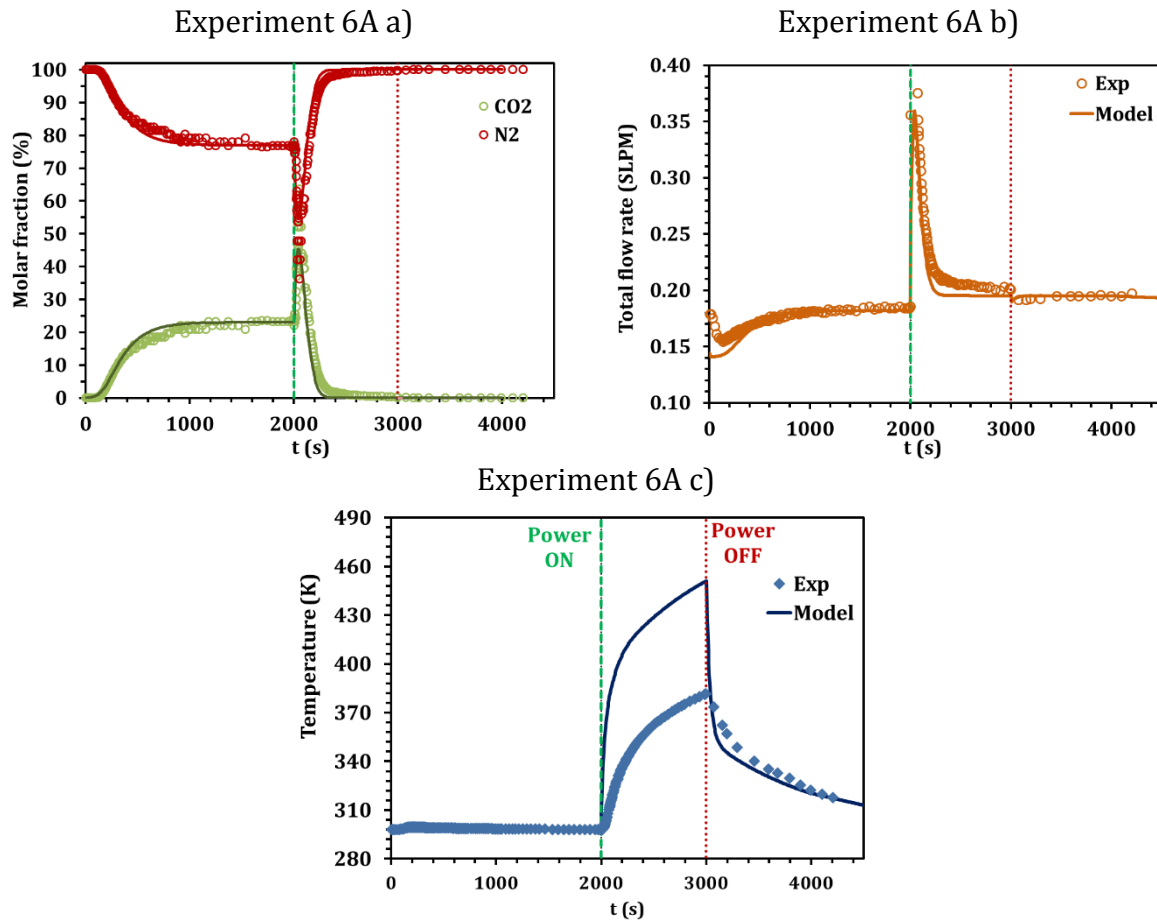
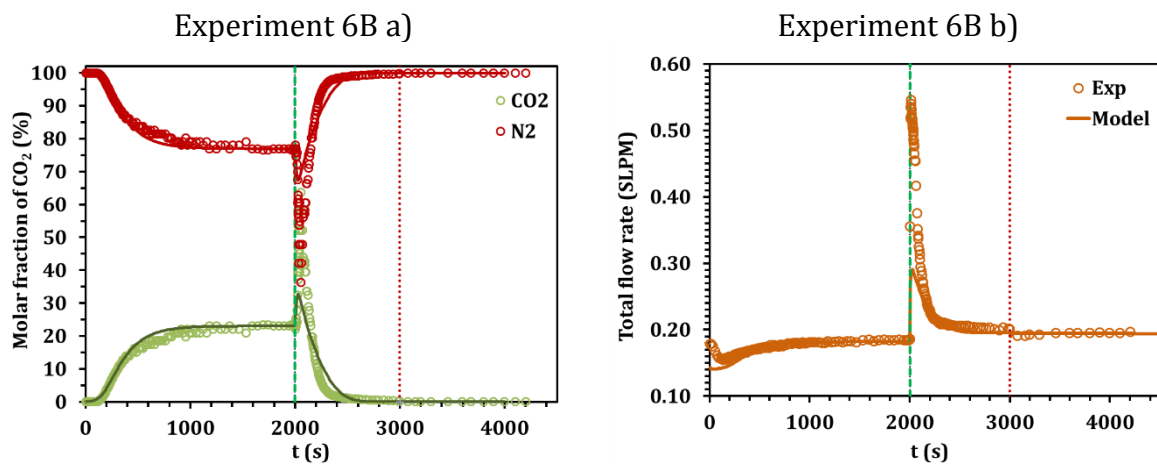


Figure 5.35. Breakthrough curve results of experiment 6A with 70%AC-30%13X pellets for inlet total pressure of 1.32 bar at 298 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.



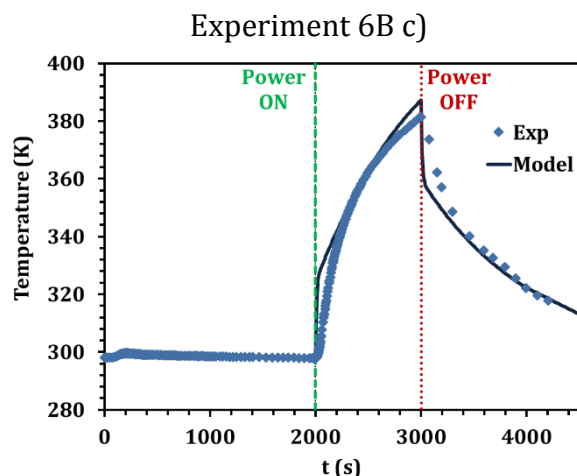


Figure 5.36. Breakthrough curve results of experiment 6B with 70%AC-30%13X pellets for inlet total pressure of 1.32 bar at 298 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

The results of the experiment 6 shows a clear effect of electrification in the adsorbent regeneration because after 1000 s, the molar fraction of CO₂ is equal to 0, while in experiment 5, the total regeneration occurs after 2500 s of the desorption step. This effect presents exactly the advantage of the use of electrification in the adsorbent.

For this case, also two simulations are presented, as again, if the molar fraction and molar flow rate are well represented, it is impossible to predict the temperature history and vice-versa.

Experimentally, two results (molar fraction and molar flow rate), measured independently by two different equipments, are in agreement, suggesting that these represent the real behaviour of the system and that for these packing some problem occurred with the thermocouple acquisition.

Transport parameters values used in the simulations are given in Table 5.14.

Table 5.14. Transport parameters values used in the simulations of the breakthrough experiments with the 70%AC-30%13X pellets.

Experiment	Exp.1 He Heat	Exp.2 CO ₂ /He	Exp.3 CO ₂ /He Heat (Exp A/B)	Exp.4 N ₂ Heat	Exp.5 CO ₂ /N ₂	Exp.6 CO ₂ /N ₂ Heat (Exp A/B)
$D_{p,i} \times 10^6$ (m ² ·s ⁻¹)	He: 8.9	CO ₂ : 2.7 He: 7.0	CO ₂ : 2.7 He: 7.0	N ₂ : 3.4	CO ₂ : 2.4 N ₂ : 2.7	CO ₂ : 2.4 N ₂ : 2.7
$D_{c,i} \times 10^7$ (m ² ·s ⁻¹)	---	CO ₂ : 1.32	CO ₂ : 1.32	N ₂ : 19.80	CO ₂ : 1.32 N ₂ : 19.80	CO ₂ : 1.32 N ₂ : 19.80
$D_{ax} \times 10^5$ (m ² ·s ⁻¹)	9.8	5.0	4.9	6.0	5.7	4.4
k_f (m·s ⁻¹)	0.11	0.04	0.04	0.06	0.02	0.02
h_f (W·m ⁻² ·K ⁻¹)	146	94	84	30	27	80
h_w (W·m ⁻² ·K ⁻¹)	2.6	120	A: 2 B: 200	5	80	A: 2 B: 80
U (W·m ⁻² ·K ⁻¹)	5	50	A: 5 B: 30	5	20	A: 5 B: 20
I (A)	0.04	-	A: 0.07 B: 0.08	0.11	-	A: 0.08 B: 1.00

5.5.4 50%AC-50%13X PELLETS

The results of the experiments performed with 50%AC-50%13X pellets are presented in this section.

In experiment 1, the pellets were submitted to an electric current between 200 s (power on) and 1100 s (power off) while a stream of helium was fed to the column. The results are shown in Figure 5.37.

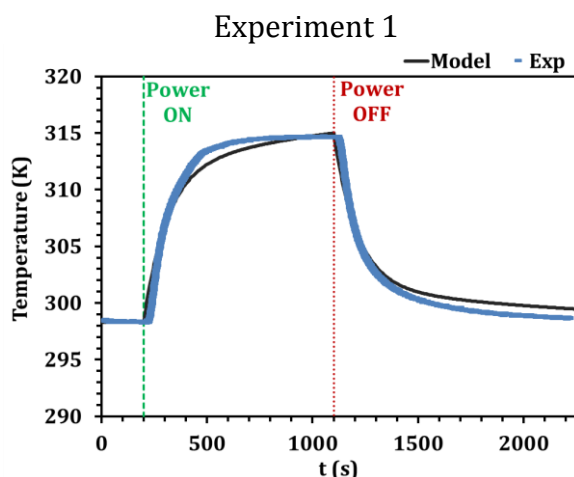
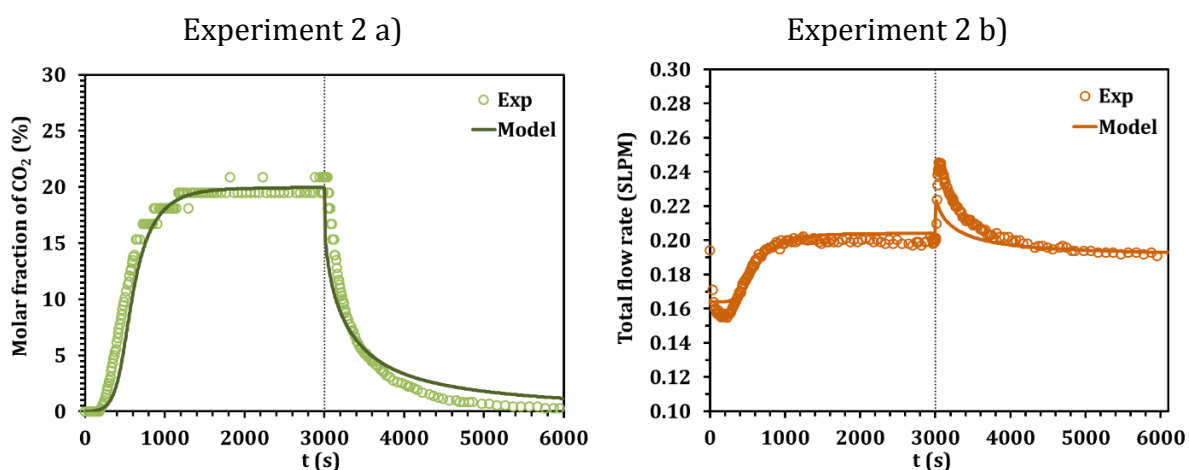


Figure 5.37. Results of experiment 1 with 50%AC-50%13X pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

As observed in Figure 5.37, the temperature of the pellets increased until 315 K in a period of 910 s, approximately. The temperature increase occurred mainly in the initial 300 s, and after that time the temperature remained almost constant

In experiment 2, a single breakthrough curve with carbon dioxide was carried out and the results are presented in Figure 5.38.



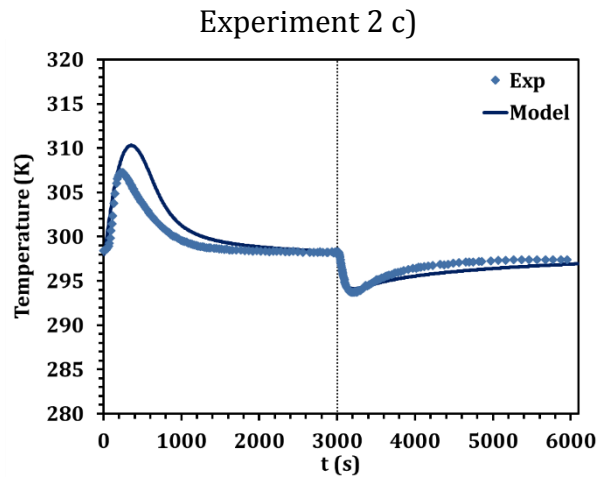
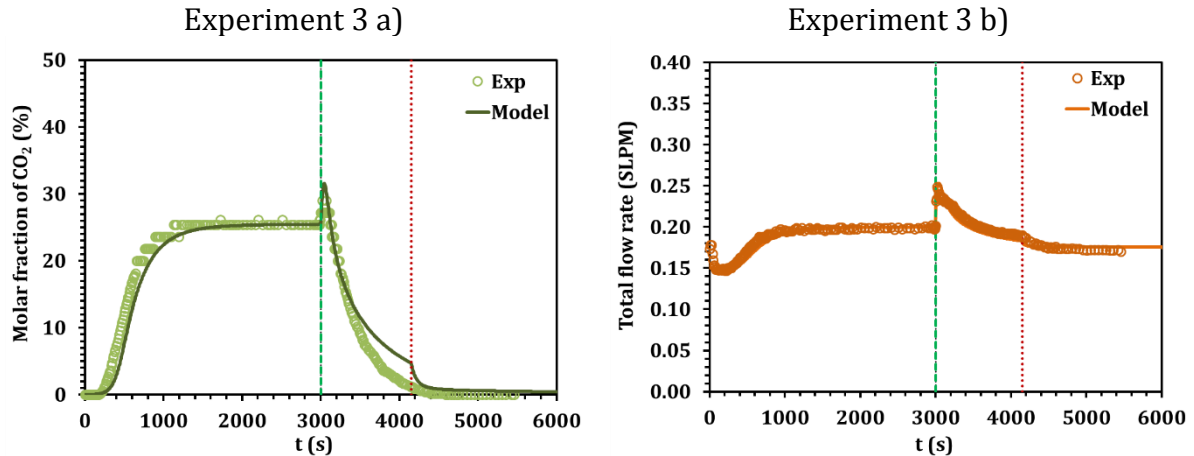


Figure 5.38. Breakthrough curve results of experiment 2 with 50%AC-50%13X pellets for inlet total pressure of 1.30 bar at 298 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

The results of experiment 3 can be observed in Figure 5.39, and it corresponds to a single breakthrough curve with carbon dioxide and electrification of the pellets during the desorption step.



Experiment 3 c)

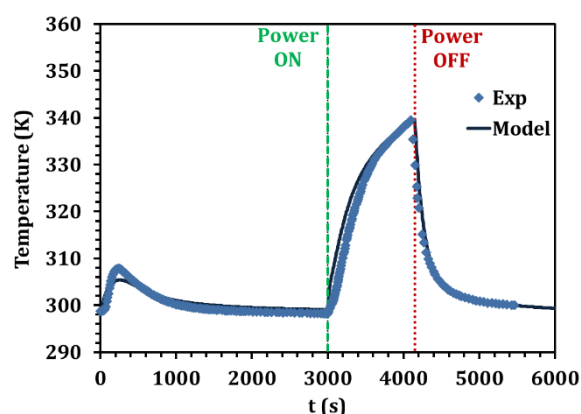


Figure 5.39. Breakthrough curve results of experiment 3 with 50%AC-50%13X pellets for inlet total pressure of 1.50 bar at 299 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

Figure 5.38 and Figure 5.39 demonstrated that the CO₂ is totally removed from the adsorbent after 3000 s and 1500 s, respectively, for experiment 3 (without electrification) and experiment 4 (with electrification). A large difference in the desorption step is obtained, although the temperature was increased only until 340 K and the electrification occurred during 1000 s.

In experiment 4, an electric current was applied at the adsorbent material between 230 s and 930 s.

Experiment 4

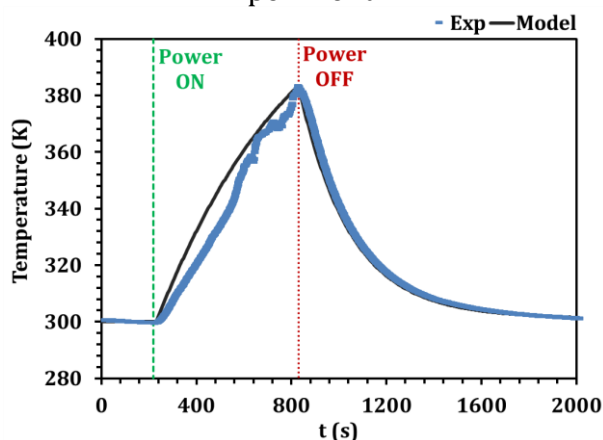


Figure 5.40. Results of experiment 4 with 50%AC-50%13X pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

In an ambient with nitrogen, the 50%AC-50%13X pellets reached a temperature of 380 K in 700 s, approximately. The temperature presented a continuous increase during the electrification, but at the 930 s, the electrification was turn off due to experimental limitations, as the O-rings used in the column support temperatures until 400 K, approximately.

Experiment 5 was carried out using a binary CO_2/N_2 feed stream. Figure 5.41 shows the results of this experiment.

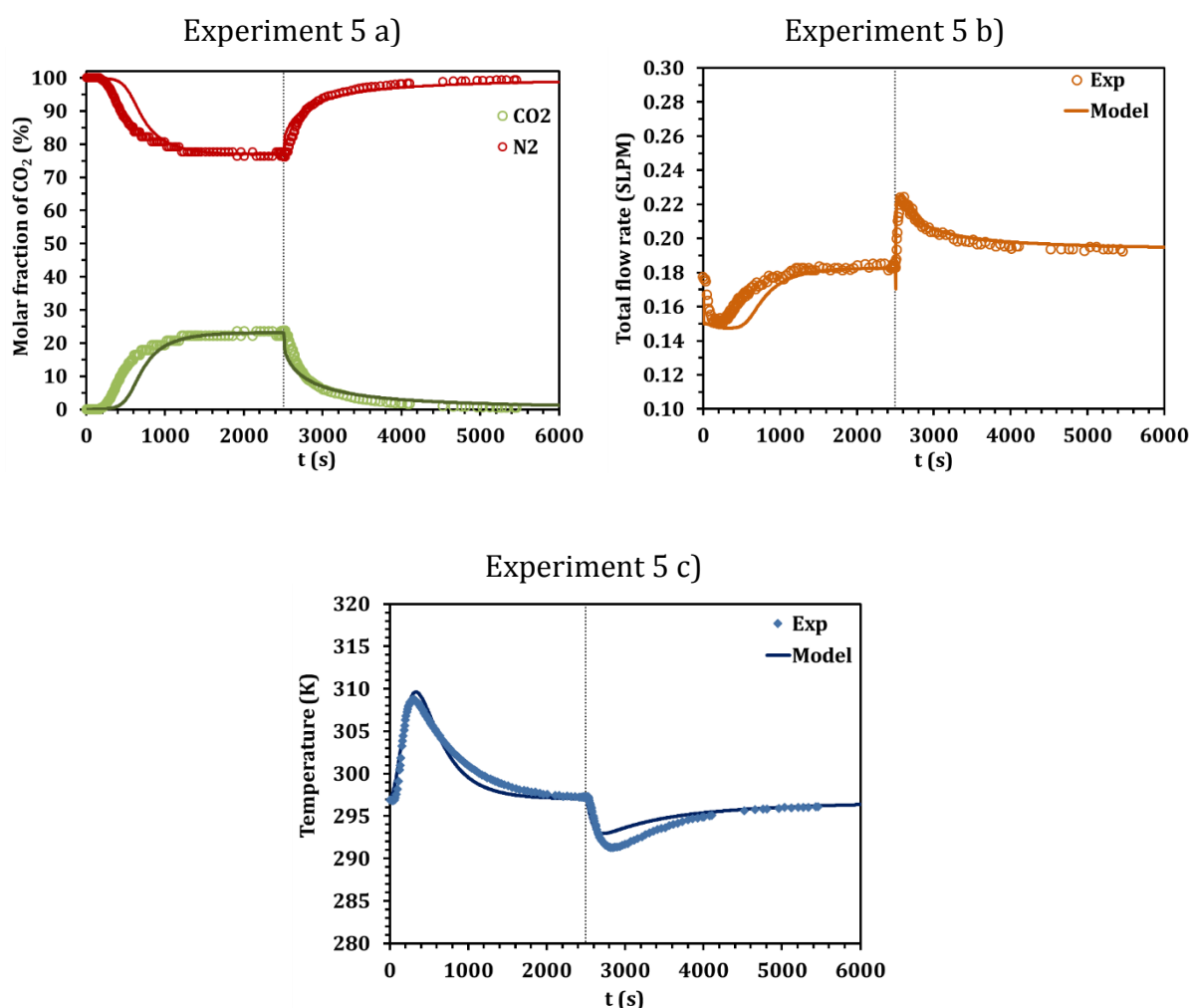


Figure 5.41. Breakthrough curve results of experiment 5 with 50%AC-50%13X pellets for inlet total pressure of 1.32 bar at 297 K: CO_2 molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

A slight difference between experimental data and simulation results in CO_2 molar fraction can be observed. The simulation predicts a higher adsorption capacity of the adsorbent than the one observed experimentally. This difference may be due to the

different conditions employed for adsorbent activation in the Rubotherm set-up and in the fixed bed set-up. In the first case, the activation is done under vacuum at 573 K overnight. In the second one, under a flow of helium at 388 K during 48 hours.

The experimental results show a temperature increase of about 15 K during adsorption and the carbon dioxide molar fraction reaches almost zero after approximately 3000 s.

Experiment 6 presents the results of a binary CO_2/N_2 breakthrough experiment with electrification during 800 s in the desorption step. These results can be observed in Figure 5.42.

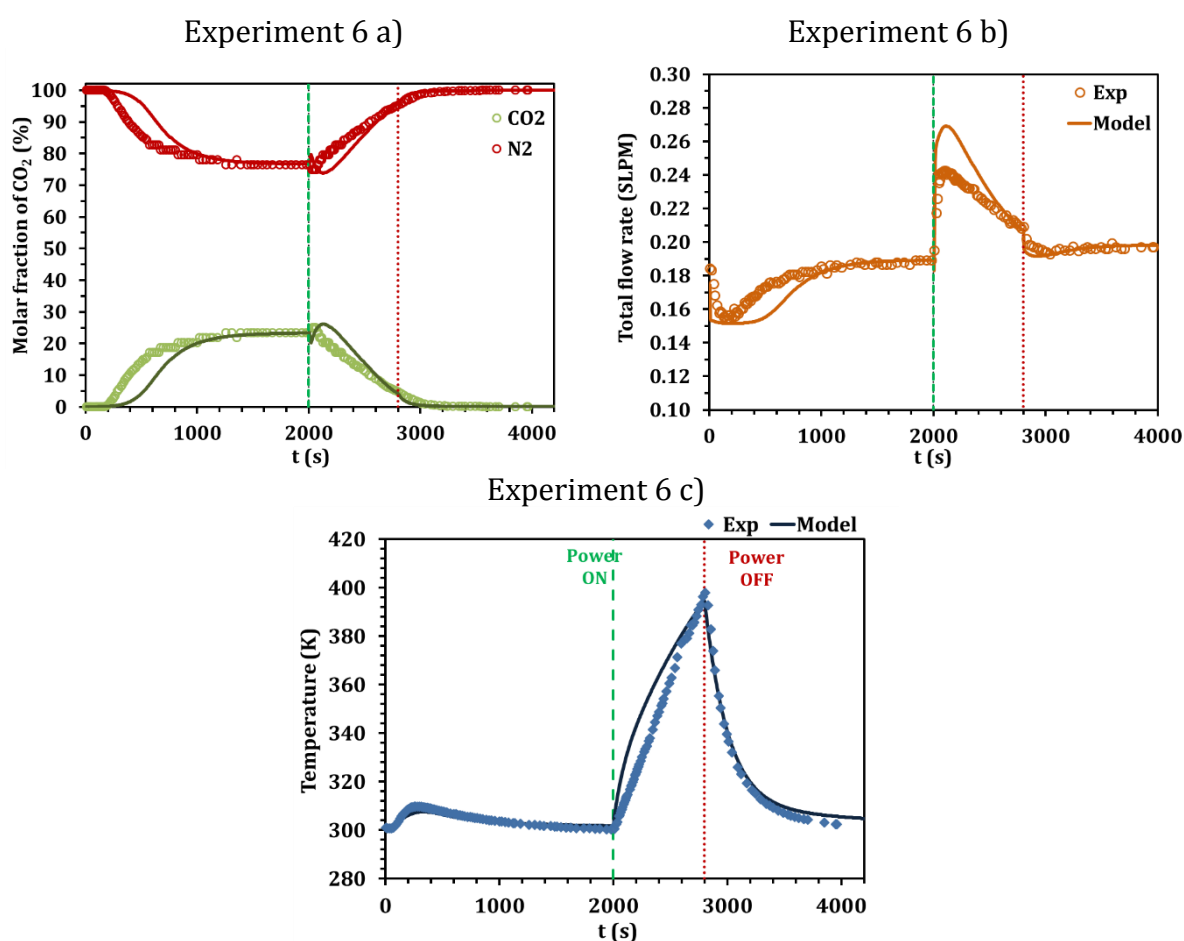


Figure 5.42. Breakthrough curve results of experiment 6 with 50%AC-50%13X pellets for inlet total pressure of 1.32 bar at 300 K: CO_2 molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

Figure 5.42 shows the same difference between experimental data and model prediction in terms of adsorption capacity. In the desorption step, the temperature reaches 400K in 800 s, resulting in a faster regeneration of the adsorbent, in about 1000 s, approximately. These results demonstrated the feasibility of these pellets to be applied in ESA process.

The values of transport parameters used are presented in Table 5.15.

Table 5.15. Transport parameters values used in the simulations of the breakthrough experiments with the 50%AC-50%13X pellets.

Experiment	Exp.1 He Heat	Exp.2 CO ₂ /He	Exp.3 CO ₂ /He Heat	Exp.4 N ₂ Heat	Exp.5 CO ₂ /N ₂	Exp.6 CO ₂ /N ₂ Heat
$D_{p,i} \times 10^6$ (m ² ·s ⁻¹)	He: 2.0	CO ₂ : 61 He: 1.9	CO ₂ : 2.7 He: 7.0	N ₂ : 2.0	CO ₂ : 2.4 N ₂ : 2.7	CO ₂ : 2.4 N ₂ : 2.7
$D_{c,i} \times 10^7$ (m ² ·s ⁻¹)	---	CO ₂ : 5.76	CO ₂ : 5.76	N ₂ : 21.45	CO ₂ : 5.76 N ₂ : 21.45	CO ₂ : 5.76 N ₂ : 21.45
$D_{ax} \times 10^5$ (m ² ·s ⁻¹)	0.1	5.5	4.9	9.9	5.0	4.9
k_f (m·s ⁻¹)	0.12	0.05	0.04	0.12	0.02	0.15
h_f (W·m ⁻² ·K ⁻¹)	146	95	86	30	27	27
h_w (W·m ⁻² ·K ⁻¹)	8	15	25	1.0	10	20
U (W·m ⁻² ·K ⁻¹)	20	20	25	5	70	12
I (A)	0.05	-	0.1	0.26	-	0.15

5.5.5 30%AC-70%13X PELLETS

Figure 5.43 reports the results of the first experiments performed with the 30%AC-70%13X pellets, in which under a stream of helium, the bed was electrified between 50 s (power on) and 1000 s (power off).

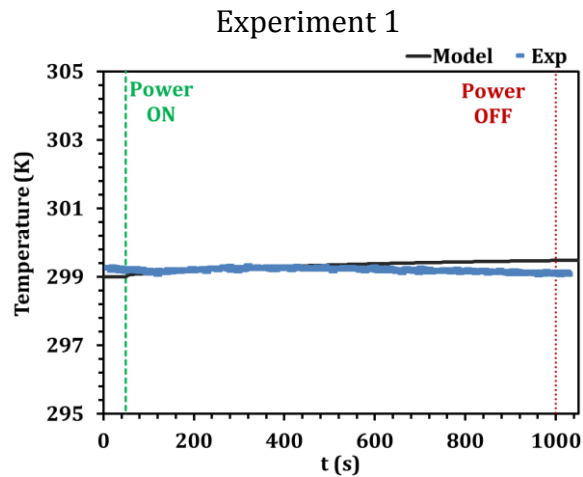
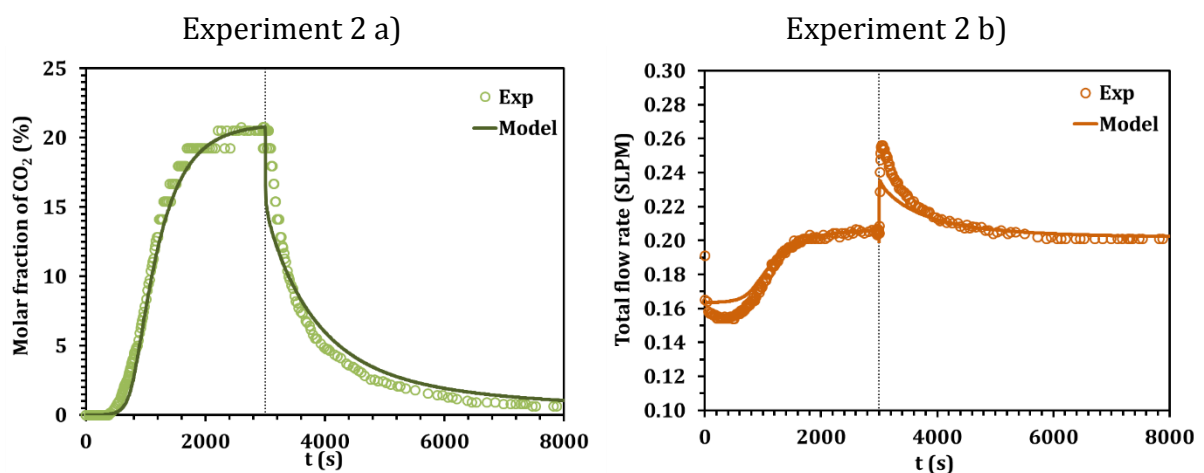


Figure 5.43. Results of experiment 1 with 30%AC-70%13X pellets: temperature history at 0.03 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

It is possible to observe in Figure 5.43 that the temperature of pellets does not increase during the 900 s of electrification, and therefore it can be concluded that these pellets with 30%AC and 70%13X are not indicated for ESA process, due to the high resistivity, i.e., poor conductivity.

For this reason, breakthrough experiments were carried out only without electrification in the desorption step.

Figure 5.44 shows the results of experiment 2, which corresponds to a single breakthrough curve with carbon dioxide in helium.



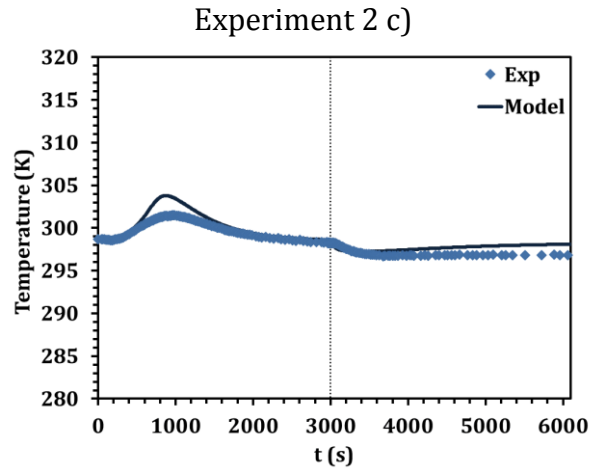
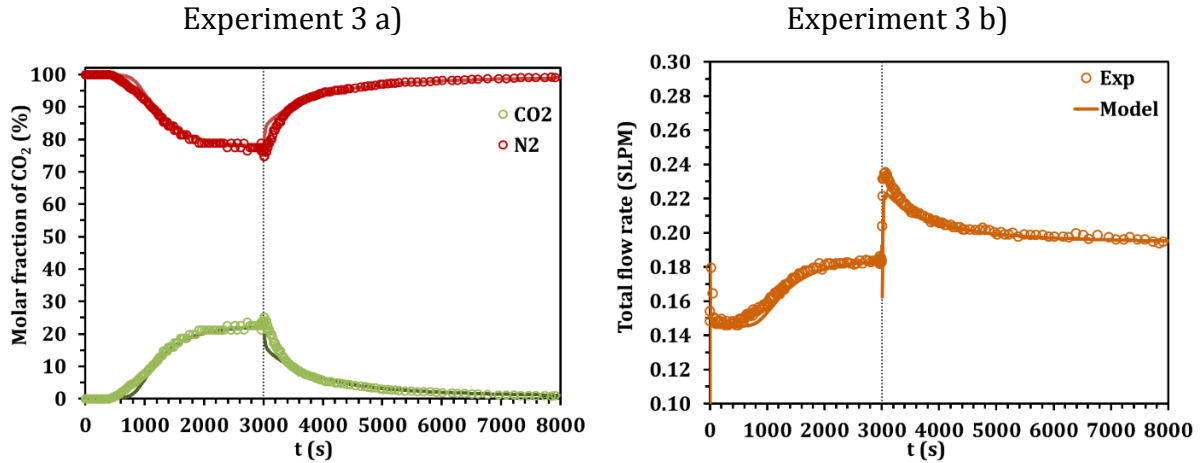


Figure 5.44. Breakthrough curve results of experiment 2 with 30%AC-70%13X pellets for inlet total pressure of 1.32 bar at 298.5 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

In experiment 3, a binary breakthrough curve with CO₂ and N₂ was performed and the results are given in Figure 5.45.



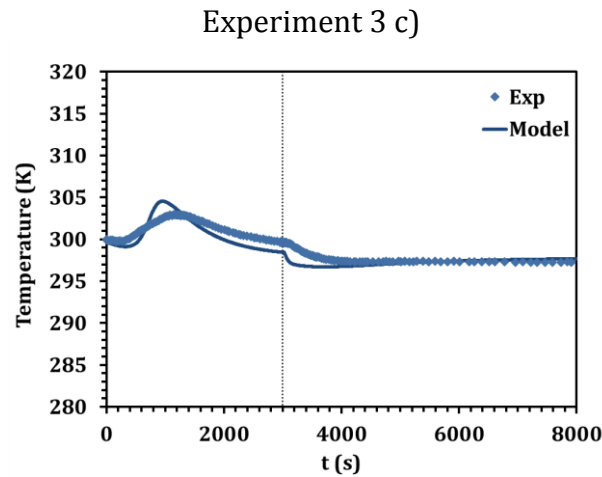


Figure 5.45. Breakthrough curve results of experiment 3 with 30%AC-70%13X pellets for inlet total pressure of 1.35 bar at 299.5 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.03 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

Table 5.16 presents the values of the transport parameters used in the simulations.

Table 5.16. Transport parameters values used in the simulations of the breakthrough experiments with the 30%AC-70%13X pellets.

Experiment	Exp.1 He Heat	Exp.2 CO ₂ /He	Exp.3 CO ₂ /N ₂
$D_{p,i} \times 10^6$ (m ² ·s ⁻¹)	2.0	CO ₂ : 62 He: 2.0	CO ₂ : 57 N ₂ : 70
$D_{c,i} \times 10^7$ (m ² ·s ⁻¹)	---	CO ₂ : 0.69	CO ₂ : 0.69 N ₂ : 38.42
$D_{ax} \times 10^5$ (m ² ·s ⁻¹)	9.9	5.6	4.8
k_f (m·s ⁻¹)	0.11	0.05	0.13
h_f (W·m ⁻² ·K ⁻¹)	146	94	28
h_w (W·m ⁻² ·K ⁻¹)	50	45	30
U (W·m ⁻² ·K ⁻¹)	40	77	40
I (A)	0.01	-	-

5.6 ESA CYCLES SIMULATIONS

To understand the feasibility of applying the developed pellets in an Electric Swing Adsorption process, some simulations were performed. The simulations were performed for two cases: one with a column packed with 100%AC pellets and another case with a column packed with 50%AC-50%13X pellets.

The model presented in section 5.3 was employed in the simulations, considering a cycle process with four steps. This cycle sequence, including four elementary steps (see Figure 5.46) can be described as:

- Step I: co-current feed, a binary mixture with 25% of CO₂ and 75% of N₂ is fed to the column, added to a stream recycled from the purge step. In this step, CO₂ is preferentially retained in the adsorbent and N₂ is obtained at the top of the column, which is used to regenerate the adsorbent during the purge step;
- Step II: electrification of the column (closed), in which an electric current is applied to the adsorbent to increase the temperature, and consequently, increasing the gas phase CO₂ composition and the pressure inside the column;
- Step III: counter-current blowdown, to depressurize the column in order to obtain a high purity stream of CO₂. As the bed is not electrified during this step, the temperature starts to decrease;
- Step IV: counter-current purge, the bed is fed with part of the purified nitrogen stream produced during step I. The CO₂ still retained in the column is desorbed to be recycled to the feed step, in order to improve the recovery of the process.

The column employed in the fixed-bed experiments and described in Table 5.8 was considered for these simulations. Feed flow rate, feed temperature and feed pressure, mass and heat transfer parameters, as well as, values of voltage and current of the power supply unit considered in the simulations are consistent with the values used in the binary CO₂/N₂ breakthrough experiments reported in section 5.5 (experiment 6), for 100%AC pellets and 50%AC-50%13X pellets, respectively.

The ESA cycle started with a co-current feed step considering that the column was filled with nitrogen. The operating parameters of the ESA simulations are also detailed in Table 5.17 for 100%AC pellets and in Table 5.19 for 50%AC-50%13X pellets.

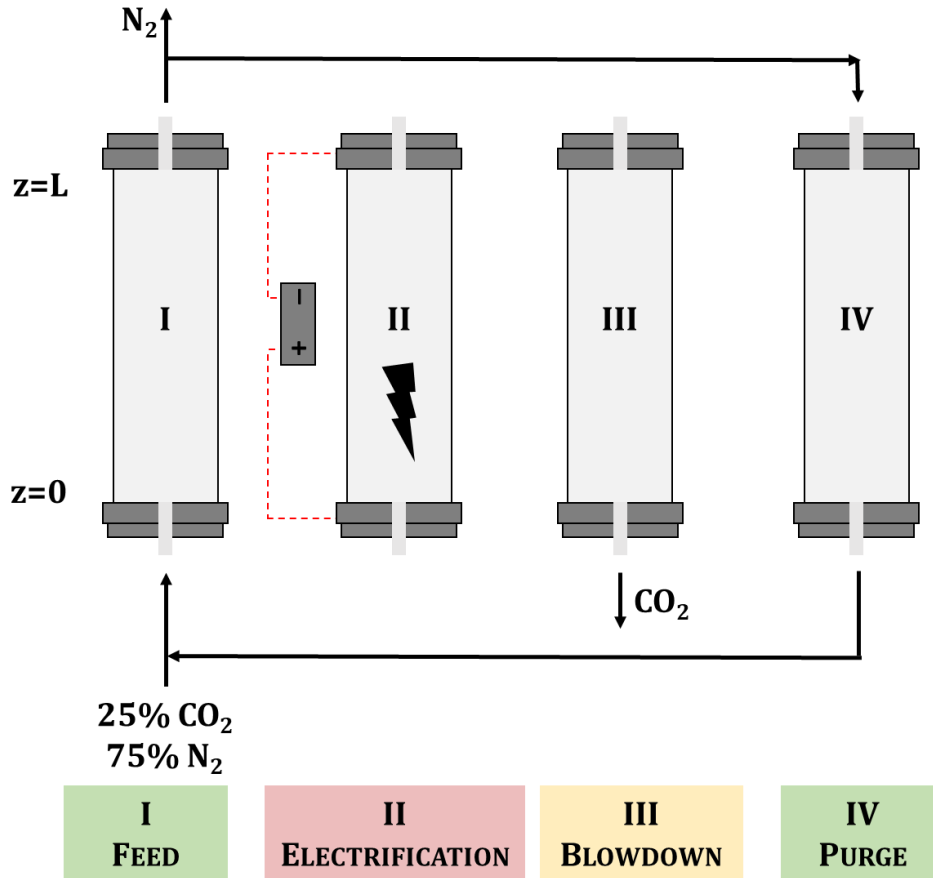


Figure 5.46. Scheme of ESA cycle designed for CO₂ capture from a stream with 25%CO₂ and 75% N₂ with four steps: I – Feed; II – Electrification; III – Blowdown; IV – Purge.

With the cycle proposed, N₂ is recovered in step I (feed) and CO₂ is recovered in step III (blowdown). The process performance is commonly evaluated in terms of purity, recovery and productivity of CO₂. In addition, N₂ purity is analysed. The referred parameters are obtained by equations 5.23 to 5.26:

$$N_2 \text{ Purity} = \frac{\int_0^{t_{feed}} C_{N_2} u_0|_{z=L} dt}{\sum_{i=1}^n \int_0^{t_{feed}} C_i u_0|_{z=L} dt} \quad 5.23$$

$$CO_2 \text{ Purity} = \frac{\int_0^{t_{blowdown}} C_{CO_2} u_0|_{z=0} dt}{\sum_{i=1}^n \int_0^{t_{blowdown}} C_i u_0|_{z=0} dt} \quad 5.24$$

$$CO_2 \text{ Recovery} = \frac{\int_0^{t_{blowdown}} C_{CO_2} u_0|_{z=0} dt}{\int_0^{t_{feed}} C_{CO_2} u_0|_{z=0} dt - \int_0^{t_{purge}} C_{CO_2} u_0|_{z=0} dt} \quad 5.25$$

$$CO_2 \text{ Productivity} = \frac{\int_0^{t_{blowdown}} C_{CO_2} u_0|_{z=0} dt}{\rho_b L t_{cycle}} \quad 5.26$$

5.6.1 100%AC PELLETS

Table 5.17 shows the conditions employed in the ESA cycle simulations using the 100%AC pellets.

Table 5.17. Conditions employed in the ESA cycle simulations with a column packed with the 100%AC pellets.

Q _{feed} (SLPM)	0.12
Q _{purge} (SLPM)	0.07
Feed composition	25% CO ₂ / 75% N ₂
P _{feed} (bar)	1.3
T _{feed} (K)	298

Run	t _{feed} (s)	t _{electrification} (s)	t _{blowdown} (s)	t _{purge} (s)
1	50	200	25	70
2	60	200	25	70
3	70	200	25	70
4	70	250	25	70
5	70	300	25	70
6	70	200	25	60
7	70	200	25	80

As observed in Table 5.17, some simulations were carried out in order to evaluate the influence of the duration of the feed, electrification and purge steps on the performance of the cycle.

Table 5.18. Performance parameters for each simulation considering a column packed with 100%AC pellets.

Run	N ₂ Purity (%)	CO ₂ Productivity (mol _{CO2} ·kg _{ads} ⁻¹ ·h ⁻¹)	Power consumption (GJ·ton _{CO2} ⁻¹)	CO ₂ Purity (%)	CO ₂ molar fraction in the recycle stream (%)	CO ₂ Recovery (%)
1	90.7	0.36	61.1	32.0	26.6	29.2
2	88.5	0.35	60.6	36.5	30.9	24.5
3	86.3	0.34	61.2	40.2	34.7	20.8
4	86.7	0.35	65.5	42.5	36.9	24.3
5	87.2	0.35	69.5	44.2	38.6	27.5
6	83.9	0.32	67.7	43.0	38.5	18.8
7	86.4	0.35	57.6	39.1	34.5	22.1

Table 5.18 shows the results of the performance parameters obtained for the 7 simulations performed. Run 1, 2 and 3 represent simulations performed with different durations of the feed step, from 50 s in run 1 to 70 s in run 3. It is verified that the CO₂ purity increases according to the increase of feed step time, as well as the CO₂ content in the recycle stream. The opposite is verified with CO₂ recovery. In addition, it is important to evaluate the purity of the nitrogen produced in the feed step. In run 1, the purity of N₂ reaches the highest value, of about 90.7%.

In run 4 and 5, different periods of electrification were tested, 250 and 300 s, and these can be compared with run 3, which was simulated using an electrification step with 200 s. The performance parameters obtained in these three simulations are very close. The difference in CO₂ purity and recovery are of around 4% and 6%, respectively. Then, 200 s is maintained for the electrification step duration in the following simulations.

Run 6 and 7 test the effect of the purge time (60 s and 80 s, respectively). It was observed that, from run 6 to run 7, the CO₂ purity and CO₂ concentration in the recycle stream decrease, although CO₂ recovery increases. However, N₂ purity increases when a higher purge time is used. Taking into account all parameters, run 1 was selected for the following discussion.

The evolution of carbon dioxide and nitrogen purities as function of the simulation cycle number is shown in Figure 5.47. It can be seen that cycle steady state is achieved after 14 cycles.

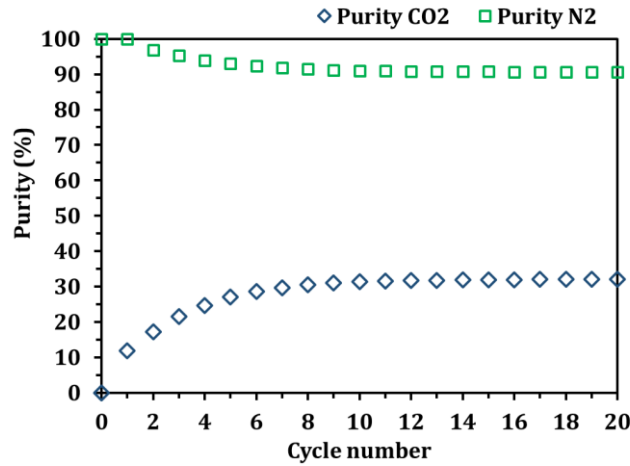


Figure 5.47. Evolution of the CO₂ and N₂ purity obtained with the simulation cycle number of run 1 for a bed packed with the 100%AC pellets.

Figure 5.48 represents the pressure history at the column outlet for the 20th cycle.

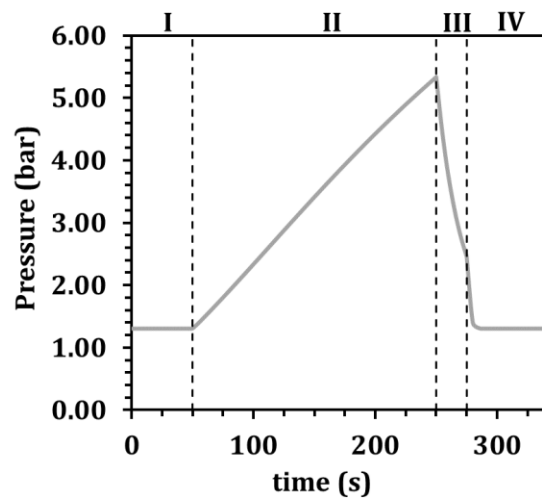


Figure 5.48. Pressure history at the column outlet during cycle 20 (vertical lines: end of each step); obtained for Run 1 with a bed packed with the 100%AC pellets.

Figure 5.49 shows the temperature history at 0.03 m also for the 20th cycle (a) and the temperature profile along the bed at the end of each step for the same cycle (b).

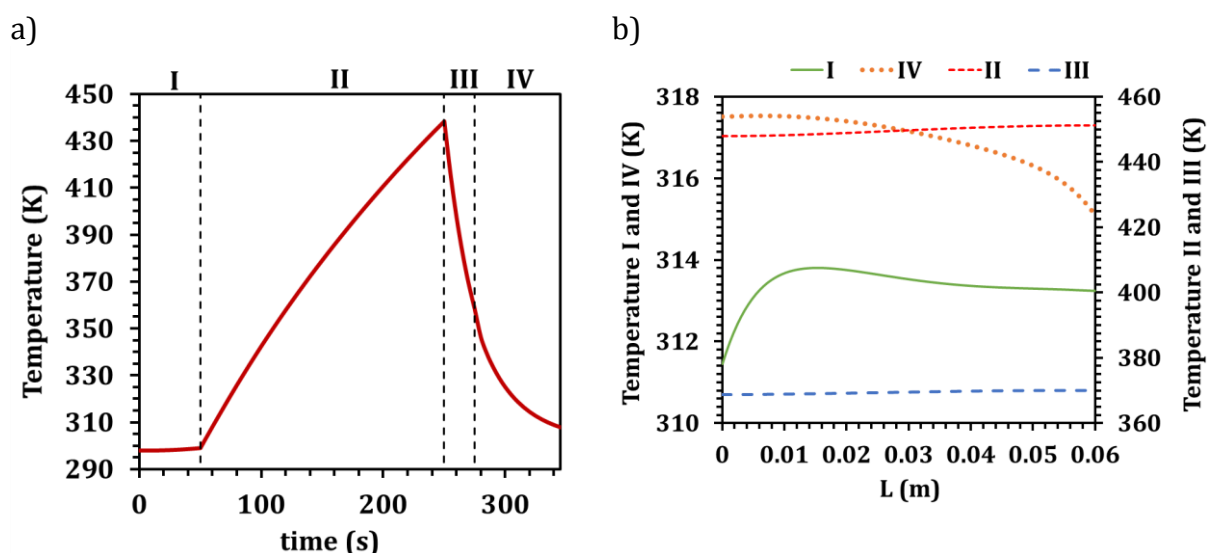


Figure 5.49. a) Temperature history at 0.03 m of the column (vertical lines: end of each step); b) temperature profiles at the end of each step for cycle 20 of run 1 for a bed packed with the 100%AC pellets.

Figure 5.48 shows that the pressure is maintained constant during the feed step and equal to 1.3 bar. Then, the closed electrification results in an increase of the pressure until about 5.2 bar. The blowdown step decreases the pressure until 2.3 bar, which is when the purge starts and the pressure reaches the initial pressure (1.3 bar).

Figure 5.49 (a) shows the temperature history along cycle number 20. During the electrification step, the temperature of the pellets reaches about 440 K in 200 seconds, representing an increase of 140 K. During the blowdown and purge steps, the temperature decreases, and at the end of purge, the temperature reaches 310 K, which is about 10 K higher than temperature of feed step. Figure 5.49 (b) shows that at the end of the feed step, the temperature varies about 1 K between $z=0$ and $z=L$. After electrification, the temperature is practically the same along the bed. During blowdown, the temperature decreases until 370 K, and it is also almost constant along the bed. In the purge step, the temperature increases between $z=L$ to $z=0$ due to the counter-current flow, and it is verified a difference of about 3 K between inlet ($z=L$) and outlet ($z=0$) of the column.

Figure 5.50 represents the molar flow rate obtained at the column outlet during cycle 20. It can be seen that during the feed step, nitrogen is the main component leaving the column, but the stream still has some carbon dioxide. During the blowdown step, a stream enriched in CO_2 is produced, but the purity obtained is quite low (32%). These results are explained by the fact that, although this material has high conductivity which

allows a marked increase in temperature in the ESA cycle, its selectivity is too low to obtain better performance parameters.

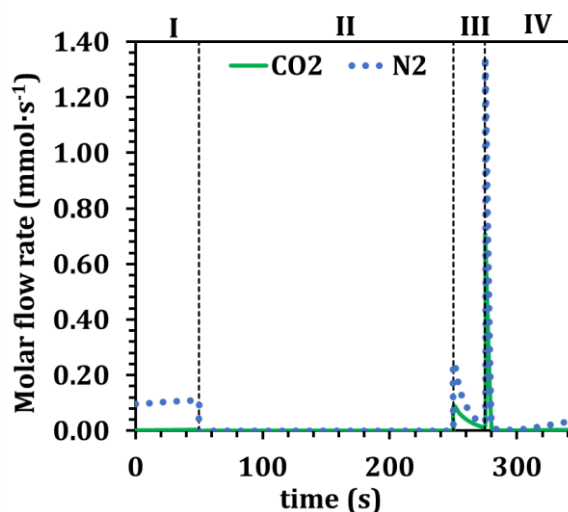


Figure 5.50. Molar flow rate of CO₂ (full line) and N₂ (dashed line) at the column outlet along the cycle 20 for a bed packed with 100%AC pellets (vertical lines: end of each step).

5.6.2 50%AC-50%13X PELLETS

Table 5.19 shows the conditions employed in the ESA cycles simulations using the 50%AC-50%13X pellets.

Table 5.19. Conditions employed in the ESA cycles simulations in a column packed with 50%AC-50%13X pellets.

Q _{feed} (SLPM)	0.12			
Q _{purge} (SLPM)	0.07			
Feed composition	25% CO ₂ / 75% N ₂			
P _{feed} (bar)	1.3			
T _{feed} (K)	298			
Run	t _{feed} (s)	t _{electrification} (s)	t _{blowdown} (s)	t _{purge} (s)
1	80	330	20	120
2	100	330	20	120
3	120	330	20	120
4	100	360	20	120
5	100	300	20	120

6	100	330	20	100
7	100	330	20	140

Once again, the effect of feed, electrification and purge steps times were analysed in terms of cycle performance (Table 5.19).

Table 5.20 presents the performance parameters obtained in steady state for each simulation performed in a column packed with 50%AC-50%13X pellets.

Table 5.20. Performance parameters for each simulation considering a column packed with 50%AC-50%13X pellets.

Run	N ₂ Purity (%)	CO ₂ Productivity (mol _{CO2} ·kg _{ads} ⁻¹ ·h ⁻¹)	Power consumption (GJ·ton _{CO2} ⁻¹)	CO ₂ Purity (%)	CO ₂ molar fraction in the recycle stream (%)	CO ₂ Recovery (%)
1	95.3	0.56	59.4	52.1	32.2	51.6
2	93.4	0.63	50.6	63.7	43.3	48.4
3	89.9	0.64	48.2	73.2	52.8	42.4
4	93.4	0.60	54.9	63.8	43.4	48.7
5	93.3	0.66	46.6	63.6	43.2	47.8
6	90.2	0.61	54.6	71.5	54.8	44.9
7	94.7	0.62	49.8	58.0	35.1	49.2

Run 1, 2 and 3 represents the evolution of the performance parameters as the feed step time increases from 80 s in run 1 to 120 s in run 3. In terms of CO₂, it is possible to observe that the increase of feed step duration increases the CO₂ purity obtained in the blowdown step over 20%, reaching a value of 73%. However, the CO₂ recovery is directly related with the obtained CO₂ purity and it decreases around 9%. When CO₂ purity increases, the CO₂ content in the recycle stream is also higher. In addition, it is important to evaluate the nitrogen purity produced in the feed step. This value decreases from 95% to 90%.

In run 4 and 5, the time of electrification step was varied between 300 and 360 s keeping the feed duration at 100 s. The values of the performance parameters obtained were practically the same, which shows that a difference of about 60 s in the electrification step is not significant. This change in the cycle is only reflected in the energy consumption that increases as the electrification time increases. Using 330 s as the time for electrification step, the duration of the purge was assessed in runs 6 and 7, being changed to 100 s and 140 s respectively. In this case, it was possible to observe that an increase in the step duration decreased the CO₂ purity (71.5% to 58.0%), with a slight increase of N₂ purity.

A more detailed analysis of the simulation results is shown below using run 2.

The evolution of carbon dioxide and nitrogen purities of the simulation cycle number 20 is shown in Figure 5.51. It can be seen that cycle steady state is achieved after 16 cycles.

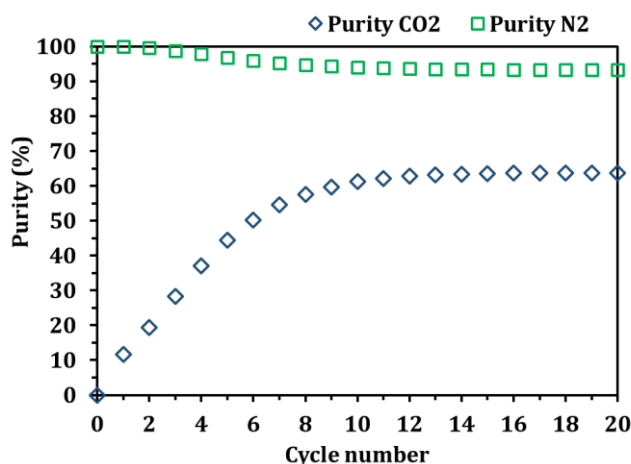


Figure 5.51. Evolution of the CO₂ and N₂ purities with the simulation cycle number of run 2 for a bed packed with 50%AC-50%13X pellets.

Figure 5.52 represents the pressure history at the column outlet for cycle 20. It shows that the pressure is constant during feed step. During the electrification step, the pressure increases until 5.5 bar, due to the high temperature reached in the column. After that, the blowdown decreases the pressure to about 3 bar, and at this moment the purge step starts. The pressure further decreases to 1.3 bar rapidly and then is kept constant at 1.3 bar.

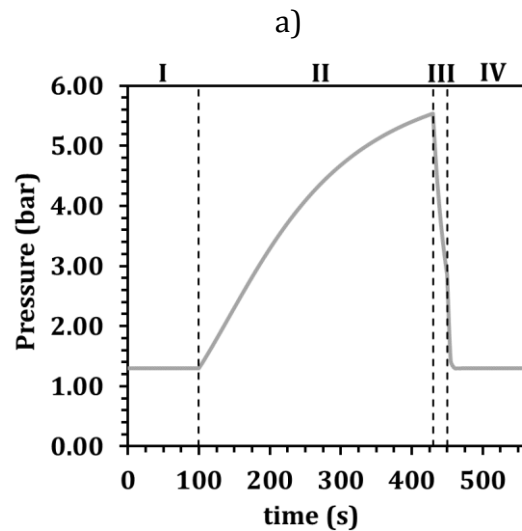


Figure 5.52. a) Pressure history at the column outlet during cycle 20 (vertical lines: end of each step); obtained for Run 2 with a bed packed with the 50%AC-50%13X pellets.

Figure 5.53 shows the temperature history at 0.03 m for cycle 20 (a) and the temperature profile at the end of each step (b).

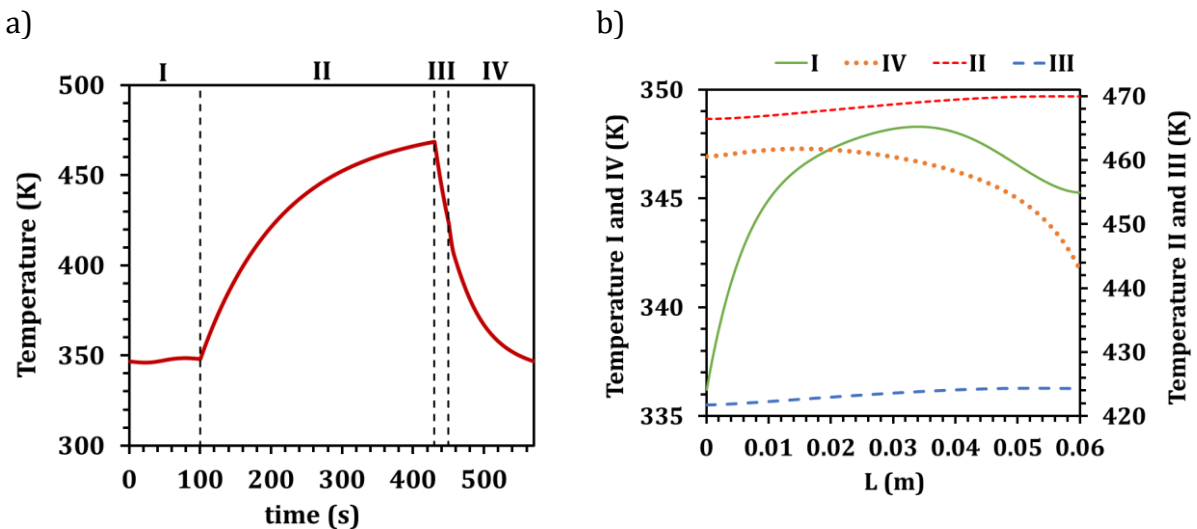


Figure 5.53. a) Temperature history at 0.03 m of the column (vertical lines: end of each step); b) temperature profiles end of each step for cycle 20 of run 2 for a bed packed with the 50%AC-50%13X pellets.

In Figure 5.53 (a), it is possible to observe that the initial temperature of the cycle is about 345 K, which results in a decrease of CO₂ adsorption capacity in the pellets, because the feed temperature of cycle 1 is not attained. A reduction of this temperature could be achieved if the duration of the purge step was higher. However, it was seen before, that the increase of the purge was detrimental in terms of performance parameters. At the end

of the electrification step, the temperature reached about 470 K, which represents an increase of 125 K in 330 s. Figure 5.53 (b) shows that at the end of the feed step, the temperature presented a profile between 336 K at $z=0$ and 345 K at $z=L$. After electrification, the temperature is practically the same along the bed. During blowdown, the temperature decreases until 420 K, and at the end of purge, the temperature reaches 348 K.

Figure 5.54 shows the molar flow rate obtained at the column outlet during cycle 2, that is in cyclic steady state.

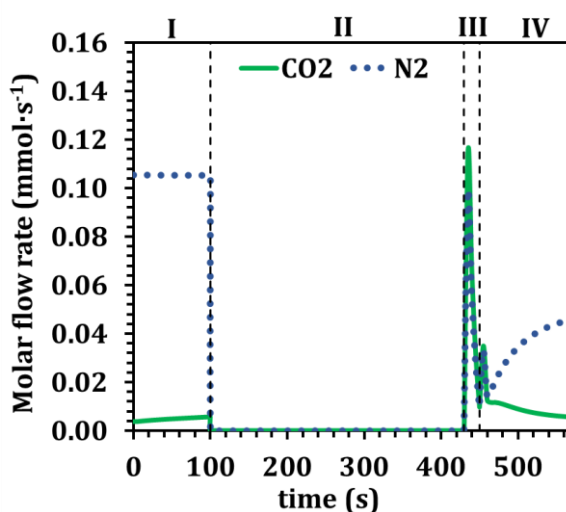


Figure 5.54. Molar flow rate of CO₂ (full line) and N₂ (dashed line) at the column outlet along cycle 20 (vertical lines: end of each step).

It can be seen that during the feed step, a purified N₂ stream is obtained and that the amount of CO₂ leaving the column increases as the step proceeds. During the electrification step the column is closed. Then, in the blowdown step, a sharp increase in the outlet molar flow rate is observed at 430 s. During the purge the CO₂ molar flow rate decreases, contrarily to N₂ flow rate, which increases until the end of cycle.

5.7 CONCLUSIONS

The development of pellets by extrusion process were carried out in order to study the viability of these adsorbents to be applied in ESA process. Four mixtures between raw materials, activated carbon and zeolite 13X, carboxymethylcellulose and water, were used to produce four different pellets: 100% of activated carbon, 70% of activated carbon and 30% of zeolite 13X, 50% of activated carbon and 50% of zeolite 13X, 30% of activated

carbon and 70% of zeolite 13X. An extensively characterization was done, demonstrating the high expected CO₂ capacity of pellets with 30% of AC and 70% of zeolite 13X.

Adsorption equilibrium isotherms of CO₂ and N₂ on the pellets were evaluated using a gravimetric method by means of a Rubotherm® microbalance. The results presented the following order of CO₂ affinity: 30%AC-70%13X > 50%AC-50%13X > 70%AC-30%13X > 100%AC, from the most adsorbed to the less adsorbed. In the opposite direction were observed the affinity of N₂, demonstrating the high selectivity of pellets, namely pellets with 30%AC-70%13X.

Single and binary breakthrough curves were performed in a fixed bed set-up. The modelling of the dynamic adsorption in a fixed bed was done. The results showed that:

- 100%AC and 70%AC-30%13X pellets: demonstrated a high performance in the electrification step, and consequently, a fast regeneration of pellets; however, the adsorption capacity of these pellets are far from the adsorbent materials with high CO₂ adsorption capacity indicated for CO₂ capture;
- 50%AC-50%13X pellets: revealed a good capacity for CO₂ capture, with a feasibility to be applied in ESA process;
- 30%AC-70%13X pellets: demonstrated high CO₂ adsorption capacity and high CO₂/N₂ selectivity; however, the heating of pellets by Joule effect failed, in the range of voltage and current of the power supply unit used, which means that in these experimental conditions, these pellets were not suitable for ESA process application.

ESA cycle simulations were performed considering a column (0.03 m of diameter and 0.06 m of length) packed with two types of pellets produced, 100%AC and 50%AC-50%13X, and a cycle with 4 steps: feed, electrification, blowdown and purge.

In the case study with 100%AC pellets, the selected simulation obtained CO₂ purity 32.0% with recovery of 29.2%. In the feed step, N₂ is produced at 90.7% of purity. This simulation presented a poor purity of CO₂ produced when 100%AC pellets are used, as expected due to the poor adsorption capacity of the material, when compared with other pellets produced. In terms of productivity, it is estimated a production of 0.36 mol_{CO₂}·kg_{ads}⁻¹·h⁻¹, representing an energy consumption of about 61.1 GJ·ton_{CO₂}⁻¹. This estimation considered that all energy supplied is used to heat the pellets without energy losses.

Using the same column packed with 50%AC-50%13X pellets, a 63.7% purity CO₂ stream was attained at the end of the blowdown step for a process CO₂ recovery of 48.4% and a productivity of 0.63 mol_{CO2}·kg_{ads}⁻¹·h⁻¹. It is possible to observe that the CO₂ concentration in the end of ESA cycle was practically increased in 40% using only about 0.010 kg of adsorbent and a very small column, which is far from columns used in industrial processes. In terms of power consumption, considering the 330 s of electrification step (cycle 20 in steady state) and the amount of CO₂ produced, 50.6 GJ·ton_{CO2}⁻¹ was consumed (without energy losses).

According to the results obtained, 50%AC-50%13X pellets are a promising material for CO₂ capture by Electric Swing Adsorption. However, some changes in the experimental set-up, as well as in the fixed bed column used (dimensions, electrodes shape and contact between the electrodes and adsorbent) should be improved.

NOMENCLATURE AND GLOSSARY

a_p	Particle external specific area	$\text{m}^2 \cdot \text{g}^{-1}$
A_{bed}	Bed area	m^2
a_{pM}	Particle specific area	$\text{m}^2 \cdot \text{g}^{-1}$
B_i	Biot number	-
C_{inlet}	Inlet gas phase concentration	$\text{mol} \cdot \text{m}^{-3}$
C_i	Gas phase concentration of component i	$\text{mol} \cdot \text{m}^{-3}$
C_p	heat capacity of the mixture at constant pressure	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\widehat{C}_p$	heat capacity at constant pressure (per mass unit)	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$C_{p,i}$	heat capacity at constant pressure of component i	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\tilde{C}_{p,s}$	solid specific heat (per mass unit)	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$\tilde{C}_{p,w}$	wall specific heat (per mass unit)	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$C_{s,i}$	concentration at the solid interface of component i	$\text{mol} \cdot \text{m}^{-3}$
C_t	total gas phase concentration	$\text{mol} \cdot \text{m}^{-3}$
$\tilde{C}_{v,ads,i}$	molar specific heat of component i in the adsorbed phase at constant volume	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$C_{v,i}$	molar specific heat of component i at constant volume	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
D_{ax}	mass axial dispersion coefficient	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{c,i}$	Crystal diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{i,j}$	Binary molecular diffusivity of component i and j	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{k,i}$	Knudsen diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$
D_m	molecular diffusivity	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{m,i}$	molecular diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{p,i}$	Pore diffusivity	$\text{m}^2 \cdot \text{s}^{-1}$
D_w	Wall internal column diameter	m
e	column wall thickness	m
h_f	heat transfer coefficient between the gas and the particle	$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$
h_w	heat transfer coefficient between the gas phase and the wall	$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$
k_g	thermal conductivity of the gas mixture	$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$
$k_{g,i}$	thermal conductivity of component i	$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$
k_f	film mass transfer coefficient	$\text{m} \cdot \text{s}^{-1}$
L_c	column length	m

m_s	adsorbent mass	kg
M_w	adsorbate molecular weight	kg·mol ⁻¹
Nu	Nusselt number	-
P	Pressure	bar
P_i	Partial pressure of component i	bar
Pr	Prandtl number	-
q_i	adsorbed amount of component i	mol·kg ⁻¹
$\bar{q}_i$	particle average adsorbed concentration	mol·kg ⁻¹
q_i^*	adsorbed concentration in equilibrium of component i	mol·kg ⁻¹
$q_{sat,i}$	adsorbent saturation capacity of component i	mol·kg ⁻¹
Q_{feed}	Feed volumetric flow rate	L·min ⁻¹
$Q_{elec-closed}$	Electrification with closed column volumetric flow rate	L·min ⁻¹
$Q_{elec-opened}$	Electrification with opened column volumetric flow rate	L·min ⁻¹
Q_{purge}	Purge volumetric flow rate	L·min ⁻¹
Re	Reynolds number	
R_g	universal gas constant	J·mol ⁻¹ ·K ⁻¹
R_p	Particle radius	m
Sc	Schmidt number	-
Sh	Sherwood number	-
t_{feed}	Feed step time	s
$t_{elec-closed}$	Electrification with closed column step time	s
$t_{elec-opened}$	Electrification with opened column step time	s
t_{purge}	Purge step time	s
T	Temperature	K
T_g	temperature of the gas phase	K
T_{inlet}	inlet temperature	K
T_s	temperature of the solid phase	K
T_w	wall temperature	K
T_∞	external temperature	K
u_0	superficial gas velocity	m·s ⁻¹
U	overall heat transfer coefficient	W·m ⁻² ·K ⁻¹
V_s	volume of the solid adsorbent	m ³ ·mol ⁻¹

y_i	molar fraction of component i	-
y_{inert}	Molar fraction of inert	-
z	axial position	m

GREEK LETTERS

α_w	Ratio of the internal surface area to the volume of the column wall	m^{-1}
α_{wl}	Ratio of the log mean surface area to the volume of the column wall	m^{-1}
ΔH	Heat of adsorption	$\text{kJ}\cdot\text{mol}^{-1}$
ΔH_i	Isosteric heat of adsorption of component i	$\text{kJ}\cdot\text{mol}^{-1}$
ε	Bed porosity	-
ε_p	particle porosity	-
λ	Heat axial dispersion coefficient	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
μ	Fluid viscosity	$\text{Pa}\cdot\text{s}$
ρ	Gas density	$\text{kg}\cdot\text{m}^{-3}$
ρ_{ap}	Apparent density	$\text{kg}\cdot\text{m}^{-3}$
ρ_b	Bulk density	$\text{kg}\cdot\text{m}^{-3}$
ρ_w	Wall density	$\text{kg}\cdot\text{m}^{-3}$

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6 3D-PRINTING HONEYCOMB MONOLITH FOR ESA PROCESS

6.1 3D-PRINTED STEPS

During the 3D-printing processes, some steps are involved. Based on the description of section 3.4.2 Chapter 3, the first step involved the design of the material to be printed. After that, the ink was developed using raw adsorbent materials, binder and solvent.

Until a printable ink and a viable design were created, some tests were carried out. The first section (6.1.1) summarizes some of the tests performed.

6.1.1 PRELIMINARY TESTS

The acquisition and installation of the 3D-printer were done during and for this work.

The first task involved the testing of the 3D-printer. Initially, these tests were done using a polymer, and then the printer was coupled with a Discov3ry for ink printing.

A Discov3ry Complete printer profile was created in Cura 3.1.0 program. This software allows converting 3D-models (.STL) into the 3D-print files (.gcode) accurately. After making some adjustments to the machine settings, such as, adjust the X, Y and Z dimensions, define the building plate shape, Cura program is prepared to open STL files and to generate gcode files.

The second task for file preparation was the study of all parameters that can be changed in the Cura program. The specifications in Cura are divided into several fields which can be adjusted to improve the quality of the printed material, such as, quality, shell, infill, material, speed, travel, cooling, support, build plate adhesion, dual extrusion, mesh fixes, special modes and experimental. Within these fields, a large number of properties can be modified, reaching a total of 355 parameters. Then, this step was very lengthy, due to the number of properties to adjust, some of which the effect was only analysed during the printing step.

In order to understand the influence of the different parameters on the printed piece, several tests were performed, modifying some properties during the printing step, or in the Cura file, iteratively.

In this section, a summary of the tested parameters is given and some figures that show the progress to the final material printed are presented.

The tests revealed that, besides the software parameters, other factors, such as nozzle diameter, nozzle shaping (conical, cylinder, curved) and nozzle material (plastic or aluminium), are very important to achieve a good printed piece. These characteristics

were defined with the acquired experience during the tests. Also, important is the quantity of water needed to prepare the ink, and consequently, the viscosity of the ink, the flow density of the ink when leaving the nozzle, which affects the applied pressure. Another critical aspect of this set of “empirical” factors was the ink adherence to the plate. The plate, fabricated in glass, caused problems on the material removal after printing. The ink could not be printed directly on the plate because after drying, the material glued to the glass and broke. To solve this problem, tracing paper was used in the plate.

After this procedure, the critical printing parameters were established: the nozzle diameter, the nozzle material, the layer height, the wall thickness, the infill density, the build plate temperature, the diameter of the filament, the enable retraction, the speed of print, the speed of infill, the speed of travel and the speed of the fans. Figure 6.1 shows the evolution between the first prints and the final tests. The initial tests (first 5 pictures) correspond to the printing of only one layer, while the last two correspond to pieces with several layers (about 5 mm height).

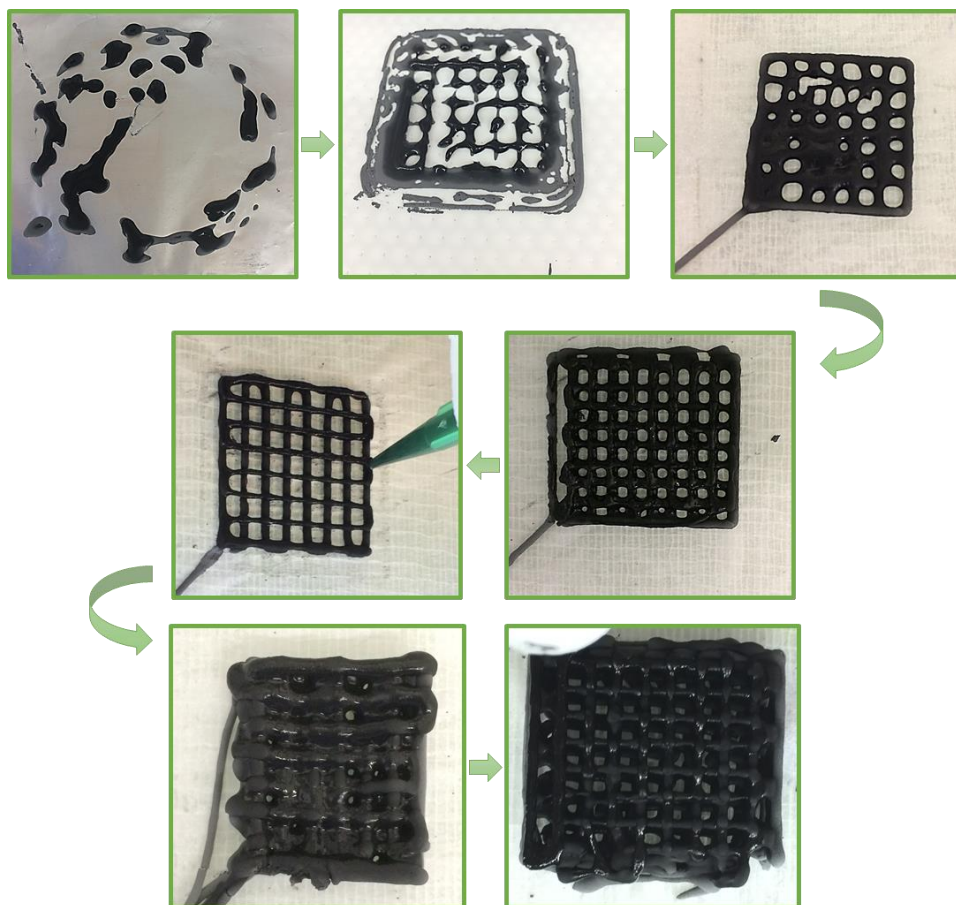


Figure 6.1. Results of some tests performed during the task of parameters optimization.

6.1.2 MONOLITH DESIGN

To create the desired monolith design, SolidWorks 2017® software was used. The material design was created and saved in STL file format. Afterwards, the file was opened in Ultimaker Cura 3.1.0 software, a G-code program was generated, and it was possible to visualize the design and define the orientation and position of the printing process. Additionally, Cura 3.1.0 was used to set the printing properties, such as print speed, layer height, wall thickness and infill density, as mentioned above.

Figure 6.2 shows the design developed on SolidWorks, which was used to print the honeycomb monoliths and Figure 6.3 shows the panel interface of the Ultimaker Cura 3.1.0 with the honeycomb monolith design.

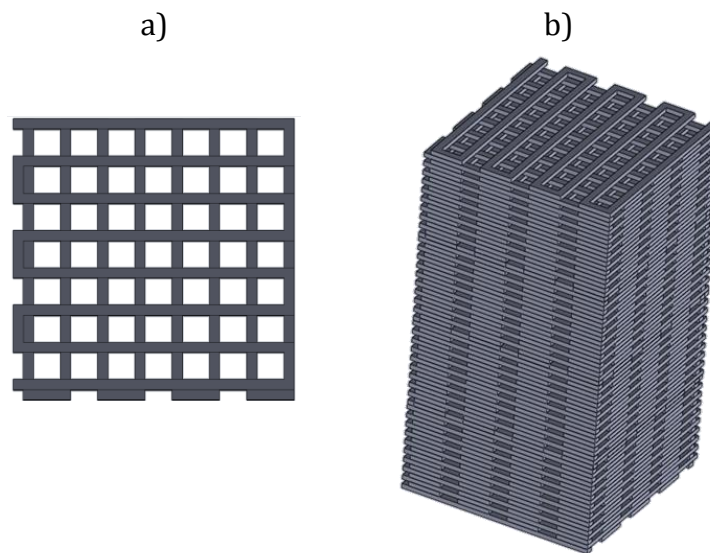


Figure 6.2. Design constructed on Solid Works (view from the top and from the front).

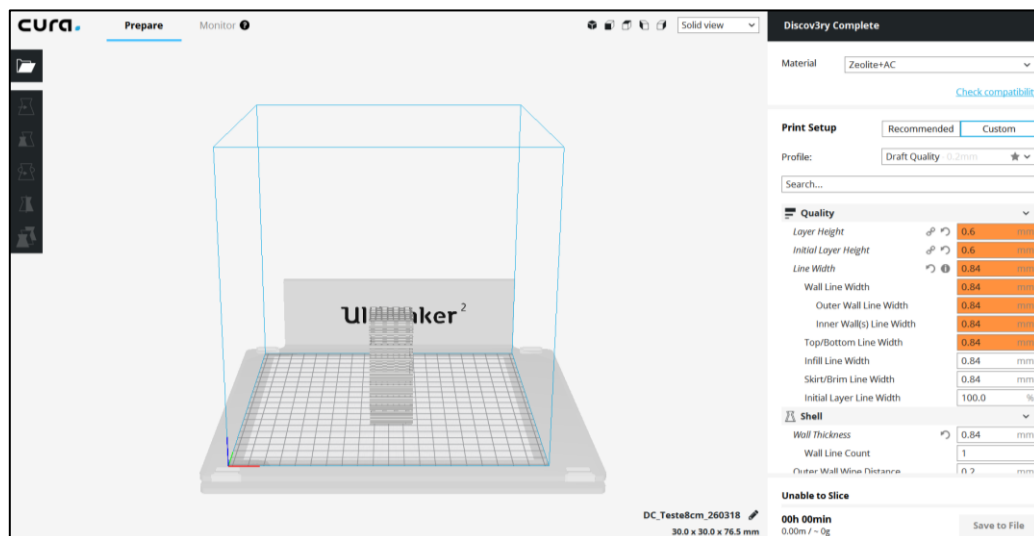


Figure 6.3. Design visualized in Ultimaker Cura 3.1.0.

6.1.3 INK PREPARATION

As described in section 3.1.1 of Chapter 3, three powders raw materials were used to prepare the ink: zeolite 13X (Chemiewerk, Kostritz) with a micropore surface area of $760 \text{ m}^2 \cdot \text{g}^{-1}$ and a particle diameter distribution between 5 and $12 \text{ }\mu\text{m}$; Maxsorb MCS-30 activated carbon (Kansai Coke and Chemicals Co Ltd) with high surface area ($> 3000 \text{ m}^2 \cdot \text{g}^{-1}$), and diameter between 60 and $150 \text{ }\mu\text{m}$; and carboxymethylcellulose (CMC, VWR) as binder.

In order to develop a suitable ink for the 3D-printing process, some tests were carried out. The most significant difference between the inks prepared was the quantity of water, to determine the ideal viscosity of the ink. This step was combined with rheological tests in order to understand the viability of the ink.

The final formulation was prepared as follows. A mixture of previously dried powders, with 21.1 g of zeolite 13X, 9.1 g of activated carbon and 1.5 g of CMC was prepared in a mixing chamber of a Multi-Lab Extruder (Caleva Process Solutions Ltd, England) during 60 minutes at 60 rpm. After that, 42 mL of deionized water was added drop by drop while mixing continuously at 70-80 rpm. At this point, the mixture presented a homogeneous and wet aspect and the ink production was completed. The mixture was immediately inserted in a syringe and placed in the Discov3ry Extruder module (Structur3D Printing, Canada) to be printed.

Figure 6.4 shows the main steps of the ink preparation.

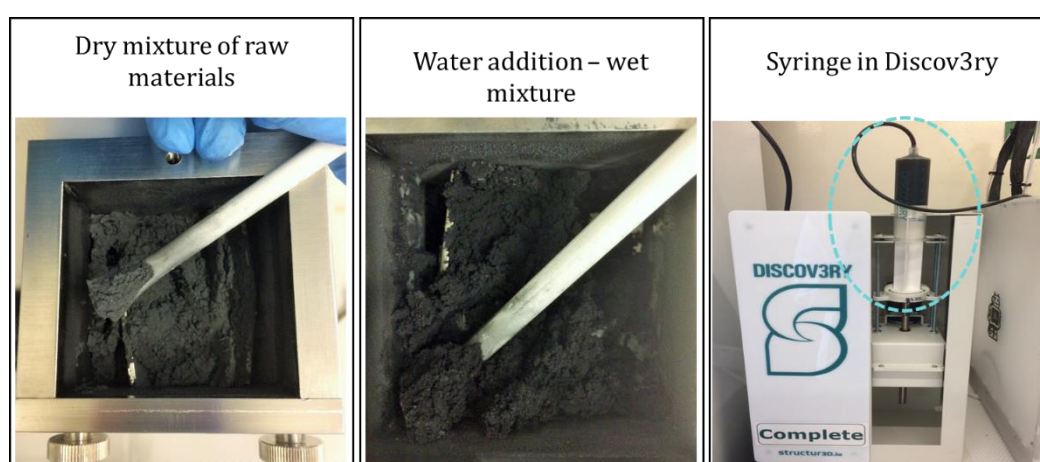


Figure 6.4. Three steps of 3D-printing ink preparation: dry powder mixture, wet paste with water addition and placing of syringe in Discov3ry.

6.1.4 RHEOLOGICAL PROPERTIES OF THE INK

As mentioned above, before the 3D-printing step, the prepared ink was analysed in terms of its rheological behaviour. The results for the final formulation are presented in this section.

Rotational parallel plate and oscillatory measurements were carried out in order to determine the rheological properties of the ink, as described in section 3.5.1 of Chapter 3.

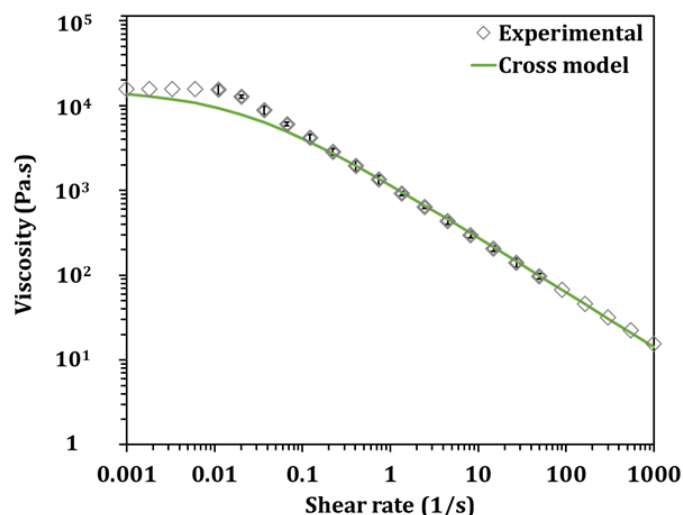


Figure 6.5. Experimental results (Test 3) of viscosity obtained in the range of shear rates between 0.001 and 1000 s^{-1} at 293 K (grey diamonds); Cross model (line); Vertical bars represent the errors between these experimental results and other two tests performed.

Three tests were performed, in which the conditions used were the same, with one exception, the shear rate range used. In Test 3, the shear rate was varied between 0.001 and 1000 s^{-1} , while for Tests 1 and 2, the shear rate was modified between 0.01 and 42 s^{-1} and 0.01 and 27 s^{-1} , respectively. These three experimental tests allowed to observe that the values of viscosity are in accordance between 0.01 and 42 s^{-1} . Figure 6.5 shows the experimental results of test 3 because this test represents the higher range of shear rates applied. Tests 1 and 2 were used to estimate the uncertainty of the results of the three tests, calculated by the standard deviation. This uncertainty is represented in Figure 6.5 by vertical error bars. Observing Figure 6.5, it can be seen that at low values of shear stress, between 0.001 and 0.01 s^{-1} , the viscosity remains constant. After 0.01 s^{-1} , it is possible to observe a linear decrease of viscosity with the shear rate increase, characteristic behavior of a pseudoplastic fluid. The cross model fitting is also shown in

Figure 6.5, and a good fit was obtained (equation 3.7 of section 3.5.1 Chapter 3). The estimated parameters are presented in Table 6.1.

Table 6.1. Parameters of the Cross model.

Cross model	
η_0	15701 Pa.s
c	49.7 s
p	0.7

In terms of 3D-printing, the high near-zero viscosity observed, due to the high value of η_0 (15701 Pa.s), is an important characteristic commonly present in highly viscous polymeric liquids. Additionally, the exponential decrease verified in the viscosity as the shear rate increases is a typical characteristic of an ink that upholds a deposition process in printing [1]. The presence of CMC in the mixture leads to the increase of the viscosity, and a decrease of the fluidity due to its flow resistance. The rotational tests demonstrated that the ink presents a shear thinning behaviour, making it appropriate for additive manufacturing. A study reported by Ghannam *et al.* (1997) [2] presented the rheological properties of CMC solutions in a concentration range between 1–5%, and the authors demonstrated a pseudoplastic flow behaviour and viscoelastic properties at the highest tested concentrations of this polymer.

In addition to viscosity, other properties estimated were the storage modulus, G' , and the loss modulus, G'' .

Figure 6.6 shows the dependence between these two properties and the strain.

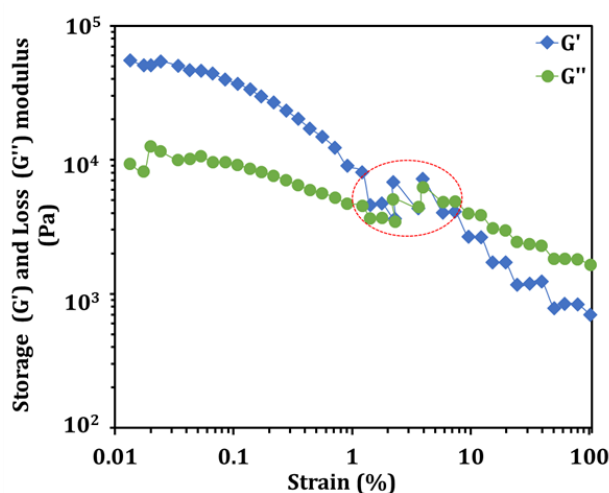


Figure 6.6. Storage modulus (G') and loss modulus (G'') of the ink obtained in the oscillatory test.

Figure 6.6 shows a decrease of the storage modulus and the loss modulus with increasing strain. For low strain percentages ($< 0.1\%$), a plateau for G' and G'' is verified, corresponding to about 50 and 13 kPa, respectively. After this value, both moduli decreased until 3.5 – 4.5 kPa, approximately, for about 1 to 7% of strain (red circle in Figure 6.6). These strain values correspond to shear stress values between 100 and 300 Pa. Until this point, the storage modulus is higher than the loss modulus, indicating that the elastic behaviour is the dominant effect. In addition, at low strain values, the difference between both moduli is higher, and decreases as the strain values increases, meaning a shift from “solid-like” to “liquid-like” fluid. From this point on, G'' is higher than G' until the end of the experience. Therefore, for strain values higher than 10%, the viscous behaviour is the dominant effect. In terms of fluid structure this means that, when the external force is smaller than the molecular/inter particular forces, G' is larger than G'' , and the material is capable of storing some energy, and it should be able to return to the initial configuration. The ink can be denominated as an elastic solid. When the applied external force is higher than the microstructure strength, the mechanical energy given to the material is dissipated and the material flows, and values of G'' larger than G' are obtained. Under these conditions, the ink can be defined as a liquid. With these two different behaviours, the ink can be denominated as a viscoelastic fluid.

During the printing process, high values of storage modulus at low strain values result in high resistance against deformation. However, increasing the strain or stress, decreases this resistance. This behaviour can be related to the path of the ink along and after the needle. First, the raw materials and the binder chains are under high stress and are aligned along the flow direction within the needle, which is the piece with a smaller transversal section. After leaving the needle, due to the pressure drop, the alignment decreases and the chains of the ink have longer relaxation time. The use of binders is important exactly in this topic, because these particles, such as CMC, are important to prevent this relaxation behaviour.

Comparing with other research works in literature, the values obtained in this work are in accordance with other 3D-inks for printing [1]. 3D-printing does not have narrow boundaries of printable characteristics, being difficult to establish standard values for the parameters. Flexibility and printability below the maximum extrusion pressure of the printer are important characteristics that should be present in the ink. The characteristics of the ink should allow the fusion of the various printed layers without spreading. High

solid quantity in the ink is another important factor to reduce cracks from drying shrinkage and porosity after sintering [1, 3].

6.1.5 3D-PRINTED HONEYCOMB MONOLITH PRODUCTION

As mentioned above, after preparation, the ink was loaded into a syringe, which was placed in the Discov3ry Extruder module. The screw was adjusted in order to be capable of exerting the required pressure to push the ink through the syringe orifice, which was connected to a plastic tube. The ink was submitted to high pressure in order to purge the system. A conical polypropylene tip of 0.84 mm of diameter was used to extrude. Concluded this step, the STL file was opened in the 3D-printer (Ultimaker 2Plus), which was coupled to the Discov3ry Extruder module, and the printing step was initiated. The drying of each layer, during the printing process, was aided by controlling the speed and temperature of two fans placed above the nozzle. The nozzle and the plate were at room temperature. The final printed honeycomb monoliths (see Figure 6.7) [4] were dried at room temperature for 48 hours.

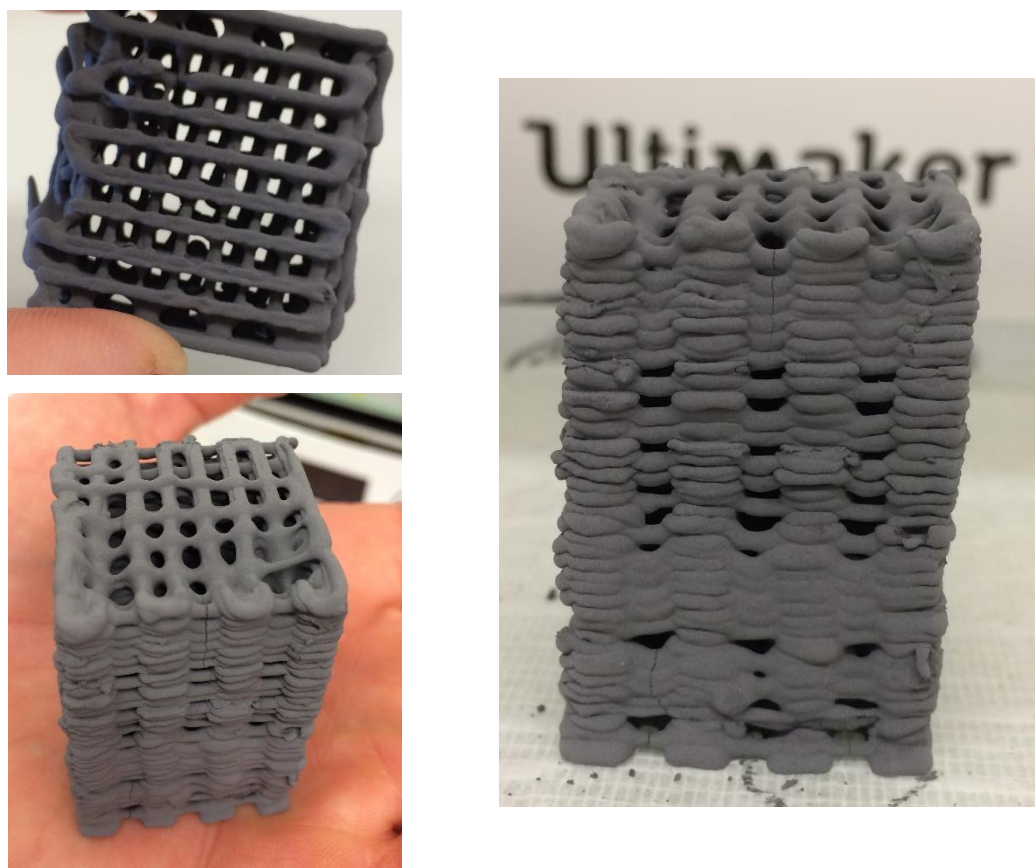


Figure 6.7. Final monolith printed.

6.2 CHARACTERIZATION

In order to not damage the final honeycomb monolith printed, additional smaller monoliths with dimensions 10×10×4 mm were printed (see Figure 6.8) with the exact same paste prepared for the final monolith, which were used for characterization (as a whole for mechanical strength evaluation or parts of the printed pieces for the remaining tests).



Figure 6.8. Monoliths printed with small dimensions for characterization tests.

6.2.1 N₂ ADSORPTION AT 77 K

Nitrogen adsorption equilibrium was measured at 77 K to estimate the specific surface area, pore volume and average pore diameter of the sample after activation at 473 K for 12h in a vacuum environment, as described in section 3.6.2 of Chapter 3.

N₂ adsorption isotherm and pore size distribution of 3D-printed honeycomb monolith are shown in Figure 6.9 a) and b), respectively.

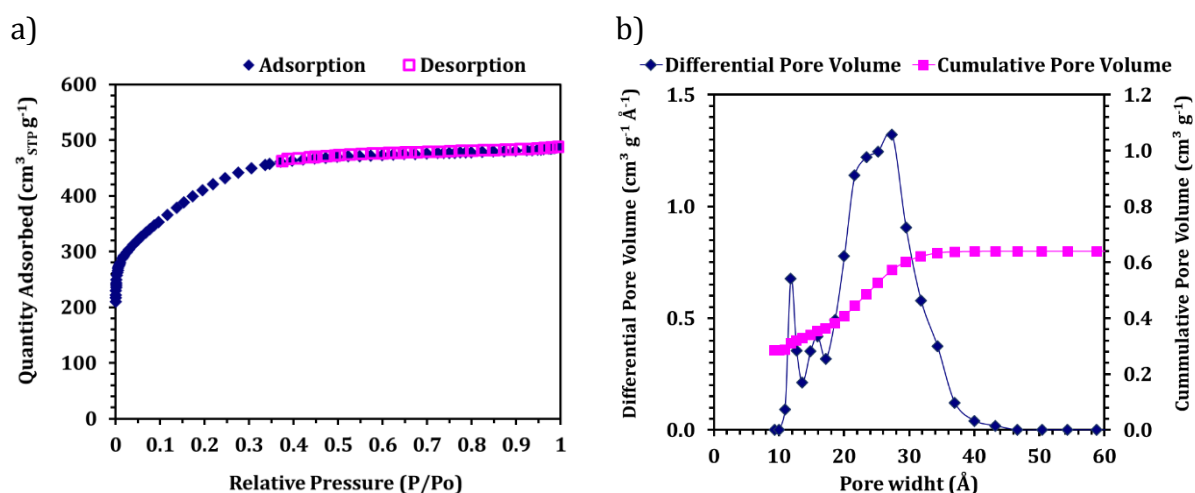


Figure 6.9. Results of a) adsorption equilibrium isotherm of N₂ at 77 K on 3D-printed honeycomb monolith (closed symbols: adsorption; open symbols: desorption); b) Pore size distribution of 3D-printed honeycomb monolith calculated from the adsorption branches of nitrogen isotherm at 77 K by the DFT method.

According to the IUPAC, the isotherm presents a type I behaviour, in line with other adsorbents developed and reported in Chapter 5, using the same raw materials and binder. It was possible to observe that the quantity adsorbed increased abruptly for pressures up to 0.05, reaching a value of about $314 \text{ cm}^3_{\text{STP}} \cdot \text{g}^{-1}$. Between P/P_0 of 0.05 and 0.4, the quantity adsorbed increased up to approximately $470 \text{ cm}^3_{\text{STP}} \cdot \text{g}^{-1}$ and then remains practically constant until $P/P_0=1$. A large amount of adsorbed N_2 at low pressures is usual in materials with a large micropore volume. The increase in adsorbed N_2 after 0.05 corresponds a typical behaviour of activated carbon, due to the presence of pores with larger sizes. Hysteresis is not observed. The Langmuir surface area of the material was determined to be $2028 \text{ m}^2 \cdot \text{g}^{-1}$.

The pore size distribution was determined using Density Functional Theory (DFT) and the total volume of micropores estimated was $0.927 \text{ cm}^3_{\text{STP}} \cdot \text{g}^{-1}$.

6.2.2 CO_2 ADSORPTION AT 273 K

Carbon dioxide adsorption isotherms were determined at 273 K to calculate the micropores volume of the adsorbent material.

Figure 6.10 presents the results obtained for the 3D-printed honeycomb monolith. Additionally, the CO_2 adsorption isotherms of the raw materials used in this work, namely 13X zeolite powder, Maxsorb activated carbon powder, as well as the two other shaped materials prepared in this work with the same activated carbon/zeolite 13X percentages, i.e. the extruded honeycomb monolith and the 30%AC-70%13X pellets, in order to have a comparison between the different materials.

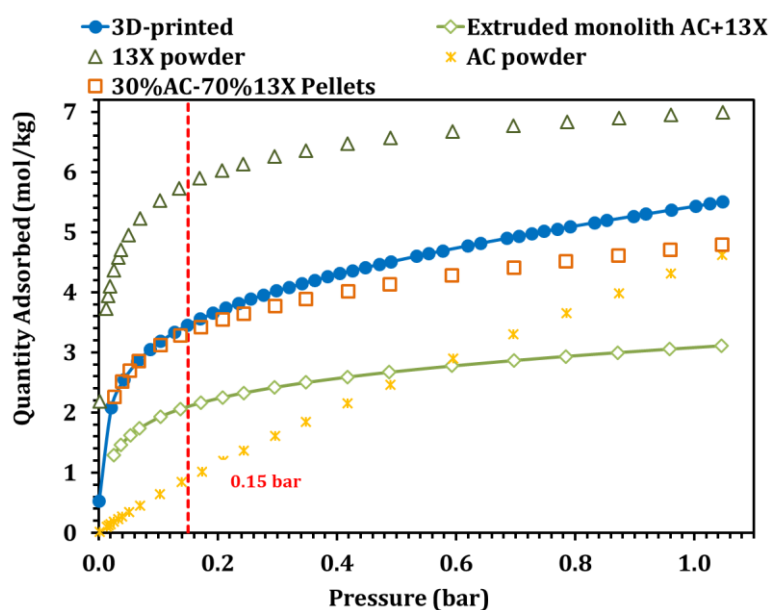


Figure 6.10. Adsorption equilibrium isotherm of CO₂ at 273 K on the 3D-printed honeycomb monolith (closed circles), on AC+13X zeolite extruded honeycomb monolith (Chapter 4) (open diamonds), on 30%AC-70%13X pellets (Chapter 5) (open squares), on maxsorb activated carbon (asterisks) and on 13 X zeolite powder (open triangles). Red dashed line represents 0.15 bar.

The CO₂ isotherm on 3D-printed honeycomb monolith has a type I behaviour, characteristic of a microporous material. A sharp knee was observed at low pressures and the adsorption capacity continued to increase at higher values of pressures, but on a smaller scale, characteristic of the activated carbon material with a presence of mesoporosity.

Analysing the adsorption capacity of the different materials in Figure 6.10, using as reference value of 0.15 bar of pressure, it is possible to observe the increase in adsorption capacity of the 3D-printed material when compared to the honeycomb monolith obtained by extrusion, described in Chapter 4. At 0.15 bar, the CO₂ adsorption capacity of the 3D-printed material is 3.49 mol·kg⁻¹, while the honeycomb monolith prepared by extrusion presented 2.12 mol·kg⁻¹ of capacity, representing an increase of 1.37 mol·kg⁻¹ (about 40%). A comparison with the pellets produced by extrusion with 30% of activated carbon and 70% of zeolite 13X (30%AC-70%13X pellets), shows that the adsorption capacity is practically the same at 0.15 bar, and that a small difference is verified for pressures higher than 0.50 bar. These results can be justified by the higher powders compaction during extrusion process, which does not occur in the 3D-printing technique, which can result in

an agglomeration of particles, making some crystals of zeolite and activated carbon inaccessible.

Considering the weight proportion of zeolite 13X and AC in 3D-printed honeycomb monolith, it was possible to estimate the CO₂ adsorption capacity loss. At 0.15 bar, the expected value of CO₂ adsorption capacity was 4.13 mol·kg⁻¹ (considering 66.7% and 28.7% of CO₂ adsorption capacity of pure 13X zeolite and pure activated carbon, respectively). The real capacity measured in the 3D-printed material was 3.49 mol·kg⁻¹, representing a decrease of about 15%. The small loss obtained is an excellent result for adsorption capacity.

6.2.3 MERCURY INTRUSION POROSIMETRY

Mercury intrusion porosimetry was measured in a range of pressures between 0.0007 and 227.5 MPa, to determine the pore size distribution, as described in section 3.6.4 of Chapter 3.

Figure 6.11 shows the results of mercury porosimetry, presented by cumulative volume of pores and differential intrusion as function of pore size diameters.

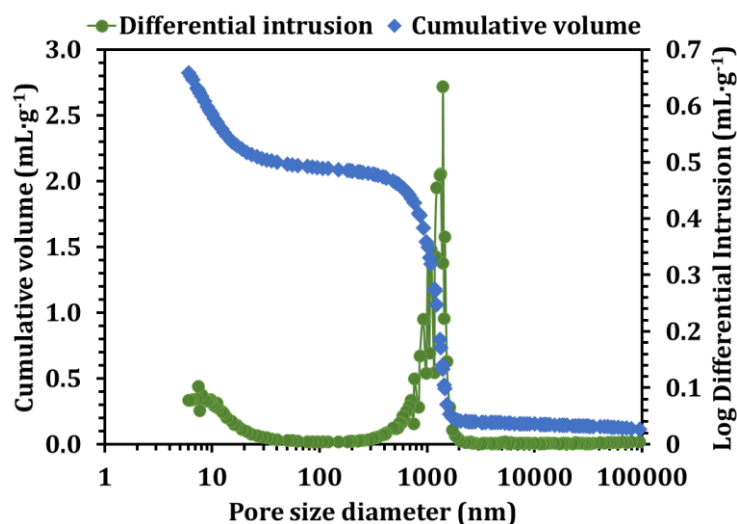


Figure 6.11. Cumulative volume of Hg adsorbed (blue diamonds) and differential intrusion of Hg adsorbed (green circles) in pores on honeycomb monolith 3D-printed.

An evident range of pore widths between 0.5 and 2 μm, approximately, was observed. The pores have a narrow distribution, indicative of uniform pore distribution.

The presence of mesopores is also observed in Figure 6.11 for pore size diameters lower than 30 nm.

6.2.4 SEM/EDS ANALYSIS

SEM and EDS analysis were performed on a 3D-printed honeycomb monolith sample and the results are presented in Figure 6.12 a) to d).

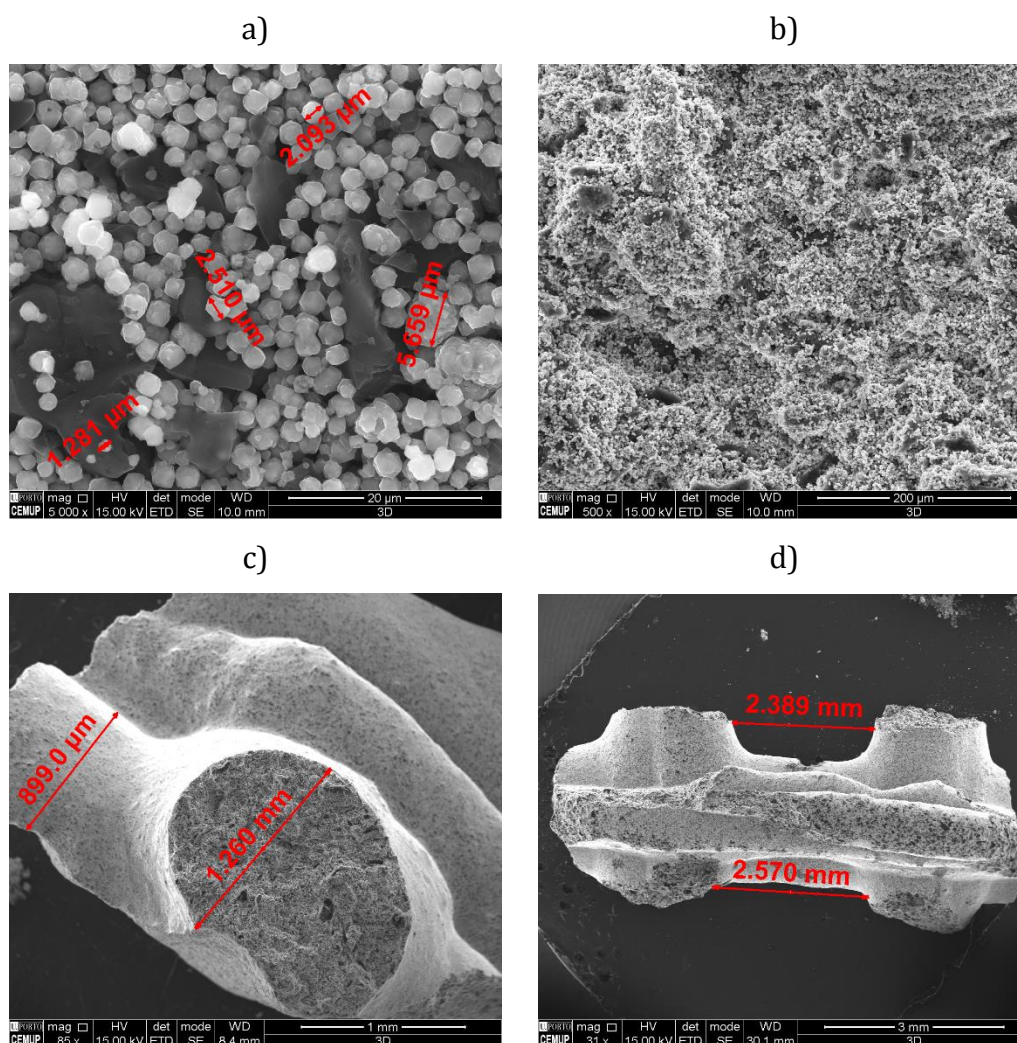


Figure 6.12. SEM photographs: of (a) fragment of the interior of a printed layer with $\times 5000$ magnification; (b) general topography of the structure sample with $\times 500$ magnification; (c) fragment of the interior of a printed layer with $\times 85$ magnification; (d) fragment of part of a printed channel with $\times 31$ magnification.

Figure 6.12 a) shows clearly the crystal structures of zeolite and amorphous particles of activated carbon. The dimensions of the 13X crystals were estimated to be between 1 and 4 μm, approximately. Some agglomerates can be observed, and in these

cases, the estimated dimension can reach up to more than 7 μm . These dimensions are in accordance with other SEM analysis of zeolite 13X reported in the literature by Zhuxian *et al.* (2016) [5], where the zeolite 13X template shows sphere-like particles with sizes of 2–3 μm . Particles of activated carbon have very different dimensions, reaching up to ten times the size of the zeolite crystals, as can be seen in Figure 6.12 a) and b). These images provide the information of raw materials distribution in the sample. A good distribution of zeolite and activated carbon was observed. In addition, Figure 6.12 b) demonstrated the existence of porosity in the material. Figure 6.12 c) represents a transversal cut in a monolith wall where it can be seen that the dimension of the wall is comprised between 0.8 and 1.3 mm. EDS analysis determined the presence of the expected elements (C, O, Na, Al, Si). Figure 6.12 d) shows part of a monolith channel with a dimension of 2.5 mm, approximately.

6.2.5 MECHANICAL STRENGTH

In order to evaluate the strength of the material, single particle axial crushing strength tests were performed on two monolith pieces with 10×10×4 mm, according to the description in section 3.6.9 of Chapter 3.

The particles did not present a total regular or smooth surface, which can influence the results. One piece crushed fully at 297 N and the other one at a slightly lower force of 215 N. This was the maximum compressive strength before failure, which can be attributed to the porosity and the microporous texture of the materials. Considering that each sample, with a cross section of 10×10 mm, has 9 square channels with 2.5×2.5 mm, approximately, corresponding to an area of crushed material of about 44 mm², and using the average value of 256 N, a strength of 5.0 MPa is obtained. Comparing with other 3D-printed monoliths published in the literature, the value obtained in this work is within the range of published values. Thakkar *et al.* (2018) [6] presented two different monoliths composed by zeolite 13X or zeolite 5A, polymer, and solvents. The printed monoliths showed a strength of 210 MPa. Another work by the same group (Thakkar *et al.* (2016) [7]), also with zeolite 13X, solvents and methylcellulose as binder, the same binder used in this work, reported a value of about 0.69 MPa. Another research work by Ugal *et al.* (2008) [8] developed uniform cylindrical pellets with 2.5 mm of diameter with zeolite 13X, kaolin, sodium silicate and solvents. The crushing tests demonstrated that the strength varied with the quantity of binder in the sample between 1.8 and 5.1 MPa

(considering the sectional area of pellet in the crushing tests was 4.9 mm² pellet) for 9 and 45% of binder content, respectively. These values are in the same order of magnitude of the value determined in this work (5 MPa). This comparison demonstrated promising properties of these 3D-printed materials for gas separation applications.

6.2.6 HEATING TESTS WITH ELECTRIC CURRENT

To study the suitability to use these monoliths for Electric Swing Adsorption applications, an electric current was applied in order to observe the Joule effect on the adsorbent. The heating experiment was conducted as demonstrated in Figure 6.13 and the procedure was described in section 3.6.8 of Chapter 3.

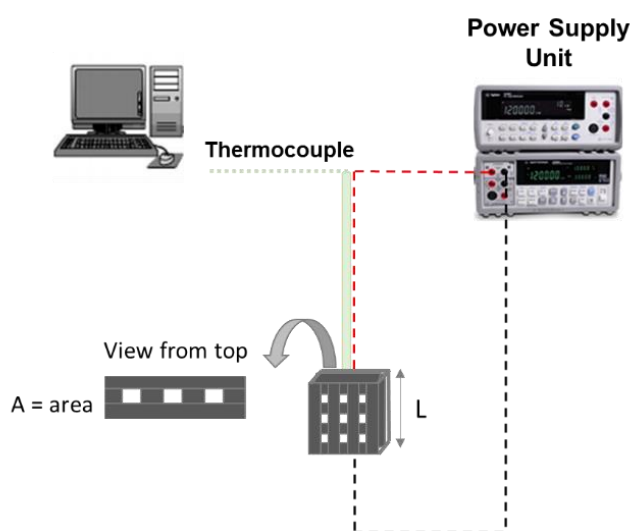


Figure 6.13. Scheme of the set-up used in heating tests measurements of the 3D-printed adsorbent.

The adsorbent was not isolated, it was maintained in contact with ambient air at the initial temperature. Two experiments were carried out with this sample, and a third experiment was done with a piece of activated carbon monolith in order to compare the heating effects. Table 6.2 shows the established and measured conditions in the experiments.

Table 6.2. Electrical conditions fixed and measured in experiments of Joule effect and respective results, maximum temperature reached and time required.

Exp	Material	Constant voltage (V)	Current measured (A)	Delivered power ^a (W)	Time to T _{MAX} (s)	T _{MAX} (maximum) (K)
1	70% 13X + 30% AC	16	0.05–0.06	1.0	484	333
2	70% 13X + 30% AC	25	0.05–0.13	3.3	180	377
3	100% AC	10	4.00–4.14	41.4	88	384

^a Considering the maximum value of watts consumed during the experiment

The results of the three experiments can be observed in Figure 6.14. The measured current during experiment 1 and 2 is reported in Figure 6.15.

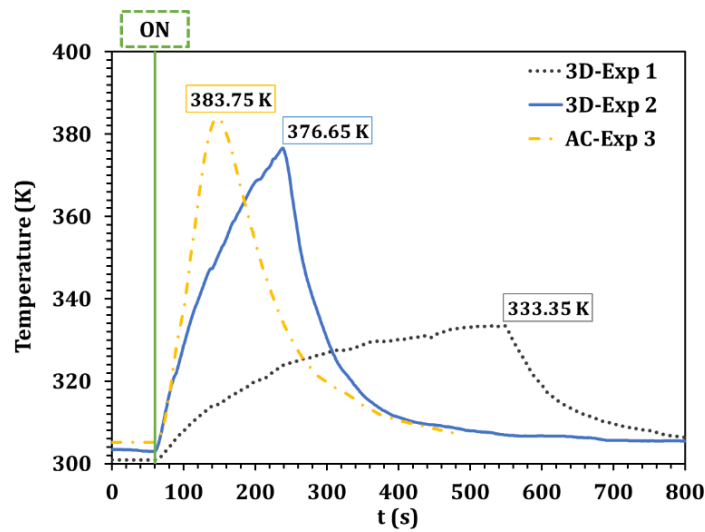


Figure 6.14. Heating measurements on the 3D-printed sample (Exp 1 and 2) and on a sample of activated carbon monolith (Exp 3). Green line at 60 min represents the moment when the power source was turned on.

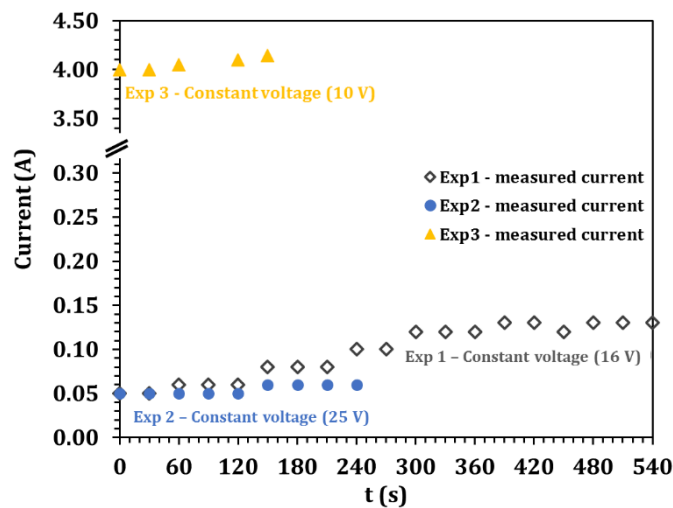


Figure 6.15. Measured current represented by diamonds for experiment 1, circles for experiment 2 and triangles for experiment 3.

Experiments 1 and 2 were carried out with a 10×10×4 mm piece of the 3D-printed honeycomb monolith, at constant voltage of 16 and 25 V, respectively. Experiment 3 was done in a piece of an activated carbon monolith from Mast Carbon® with 10 mm of height, at constant voltage of 10 V. These experiments were conducted during different periods of time, but all were conducted with the power source turned off from 0 to 60 seconds, during which the thermocouple reading represented the initial temperature of each experiment. At 60 s, the power was turned on until the maximum temperature was reached. From that moment, the power supply unit (PSU) was turned off and it was recorded the subsequent decrease in temperature.

In experiment 1, the PSU was on during 484 s, until a temperature of 333 K was reached. At this point, due to the extended time of heating, the power source was turned off. To reduce the heating time, experiment 2 was carried out at a higher voltage (25 V), and as can be seen in Figure 6.14 a higher maximum temperature was reached in shorter time, about 377 K in 180 s. In the case of activated carbon, experiment 3 showed that a more efficient heating step was obtained, reaching a temperature of 384 K in 88 s only. At this point, PSU was turned off for security, because the electric current measured was 4.14 A, and the maximum value supported by the installed alligator clips was 5 A.

According to Ohm's Law, the voltage is equal to the current intensity multiplied by the resistance. As expected, the resistance of the 3D-printed material is considerably

larger than the pure activated carbon one, around 280 Ω and 2.5 Ω respectively. In order to calculate the resistivity (ρ) of the 3D-printed material, equation 6.1 was applied:

$$R = \rho \frac{L}{A} \quad 6.1$$

where R is the resistance in ohm, L is the length and A is the cross-sectional area of the sample. Considering L as 10 mm and A as the total area (40 mm²) minus the area of 3 void spaces with 2.5 per 4 mm of dimensions (30 mm²), the calculated resistivity values are 0.28 and 0.0025 Ω m, considering the average resistance of 280 and 2.5 Ω , respectively. For this reason, the voltage needed to conduct the electric current in the 3D-printed sample is higher than in the AC sample.

6.3 MATHEMATICAL MODEL

In this chapter, 3D-printed honeycomb monolith was tested, i.e., the same shape of the material produced by extrusion and presented in Chapter 4. Then, the mathematical model used to predict the experimental data for the 3D-printed honeycomb monolith was the same, only considering some modifications related to the structure (length, weight, number and dimension of channels, between others).

The initial and boundary conditions used in the mathematical model simulation of the breakthrough curves with the honeycomb monolith by extrusion were reported in Table 4.2 of Chapter 4, and used in breakthrough experiments with 3D-printed honeycomb monolith.

The model was implemented in gProms 4.2.0 (PSE Enterprise, United Kingdom) and solved using orthogonal collocation on finite elements method (OCFEM) with second order polynomials over a uniform grid of 150 intervals.

6.4 ADSORPTION EQUILIBRIUM ISOTHERMS

In order to determine the adsorption equilibrium isotherms of CO₂ and N₂ in the 3D-printed material, the set-up described in section 3.7.1 of Chapter 3 was used.

Adsorption equilibrium data of CO₂ were determined at four different temperatures, 303, 318, 333, and 373 K in the pressure range of 0 to 1.50 bar, approximately. N₂ adsorption equilibrium isotherms were also determined at 303, 333 and 373 K in the same pressure range. The results are presented in Figure 6.16.

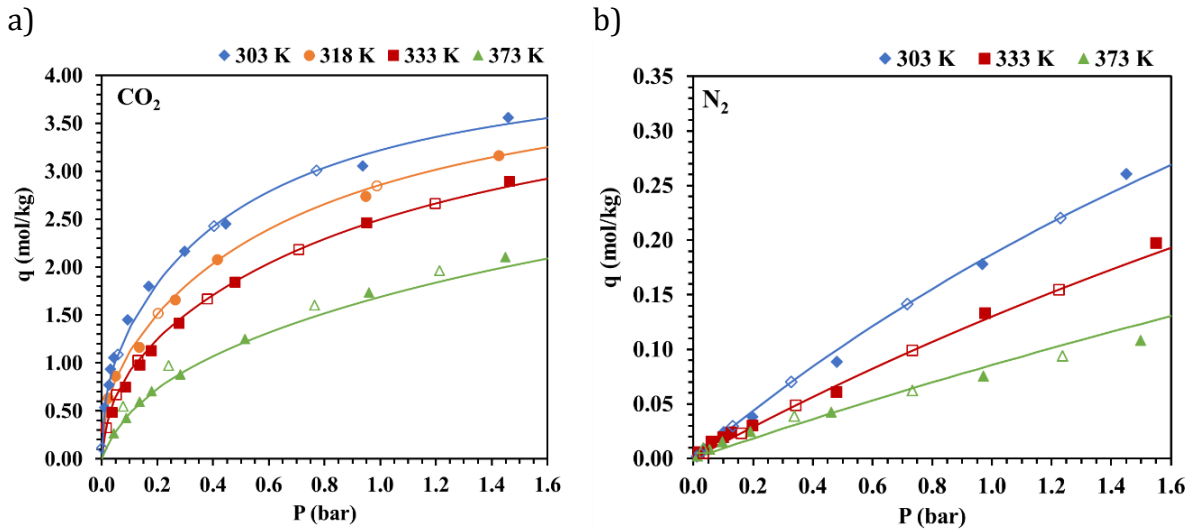


Figure 6.16. Adsorption equilibrium isotherms of a) CO₂ and b) N₂ on 3D-printed honeycomb monolith: experimental points (closed adsorption, open desorption) at 303 K (diamonds), 318 K (circles), 333 K (squares) and 373 K (triangles) and Dual-Site Langmuir isotherm fitting (lines).

The experimental data were fitted with the Dual-Site Langmuir model (equations 6.2 and 6.3):

$$q_i = q_{sat,1,i} \frac{b_{1,i}P_i}{1 + b_{1,i}P_i} + q_{sat,2,i} \frac{b_{2,i}P_i}{1 + b_{2,i}P_i} \quad 6.2$$

$$b_{k,i} = b_{0,k} \exp\left(\frac{-\Delta H_k}{R_g T}\right) \quad 6.3$$

The parameters of the Dual-Site Langmuir model were obtained for each adsorbate minimizing the sum of the squared absolute errors between the calculated and experimental values with the Excel Solver add-in. The values are given in Table 6.3.

Table 6.3. Fitting parameters for CO₂ and N₂ single component adsorption equilibrium isotherms for the Dual-Site Langmuir model on the 3D-printed material.

Species	$q_{sat,1}$ (mol·kg ⁻¹)	$q_{sat,2}$ (mol·kg ⁻¹)	$b_{0,1}$ (bar ⁻¹)	$b_{0,2}$ (bar ⁻¹)	$(-\Delta H)_1$ (kJ·mol ⁻¹)	$(-\Delta H)_2$ (kJ·mol ⁻¹)
CO ₂	3.580	0.797	2.28×10^{-4}	4.66×10^{-5}	23.0	37.2
N ₂	0.997	0.010	1.94×10^{-3}	1.00×10^{-6}	12.0	10.0

In general, a good fitting was obtained. As expected, CO₂ is the most adsorbed component, when compared with nitrogen. It is possible to verify an abrupt increase of the quantity adsorbed of CO₂ at low pressures, a characteristic behaviour of the zeolite 13X. Observing Figure 6.16, it is possible to estimate an adsorbed amount of about 1.45 mol·kg⁻¹ at 0.09 bar and 303 K of CO₂, which can be considered an excellent result for CO₂ adsorption capacity.

6.4.1 ISOSTERIC HEATS OF ADSORPTION

The experimental isosteric heats of adsorption as function of the loading can be calculated from the adsorption equilibrium isotherms results, applying the Clausius-Clapeyron (equation 6.4).

$$(-\Delta H) = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_q \quad 6.4$$

The values are presented in Figure 6.17 and also compared with the heats of adsorption obtained through the Dual-Site Langmuir isotherm fitting.

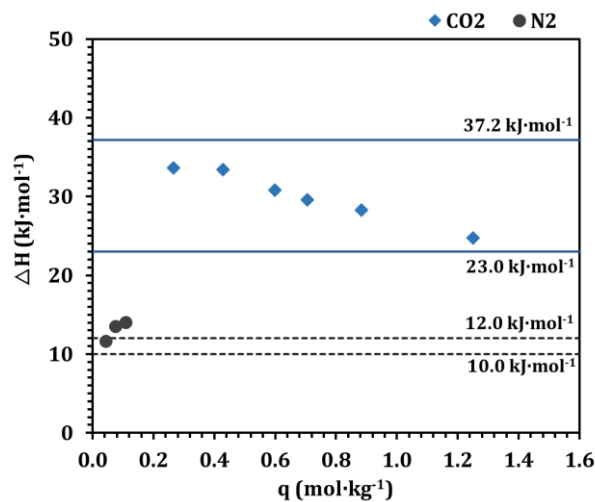


Figure 6.17. Single-component isosteric heats of adsorption on 3D-printed honeycomb monolith for CO₂ and N₂ as a function of amount adsorbed in the temperature range of 303-373 K; Lines represent the values obtained through the Dual-Site Langmuir fitting.

6.5 BREAKTHROUGH CURVE EXPERIMENTS

Breakthrough curve experiments were performed in the same lab-scale fixed-bed unit used in the experiments reported in Chapter 4 and 5, and described in section 3.9.1 of Chapter 3.

6.5.1 EXPERIMENTAL CONDITIONS

A new stainless steel column was designed and developed to pack the 3D-printing honeycomb monolith. This column has an exterior cylinder in stainless steel and an interior in teflon to ensure the safety when an electric current was applied. The internal teflon column had dimensions of 30.5×30.5×43.0 mm. The aluminium electrodes were positioned in the top and the base of the teflon, in order to promote the contact between the electrodes and the honeycomb monolith. Furthermore, the electrodes contacted only with the Teflon column, being isolated from any metallic part, protecting the passage of electric current between electrodes and stainless steel column. A small hole was done in each electrode in order to insert the electrical cable, which made the connection between the power supply unit and the electrodes. In order to prevent the escape of eventual fines of the material from the column, a net of fine mesh, made of stainless steel, was placed in the top and the base of the column in gas inlet and outlet connections. Moreover, glass wool was placed between each face of the honeycomb monolith and the end and the top of the structure.

The temperature of the gas phase was measured in the middle of the honeycomb monolith by a thermocouple. The column design can be observed in Figure 6.18.

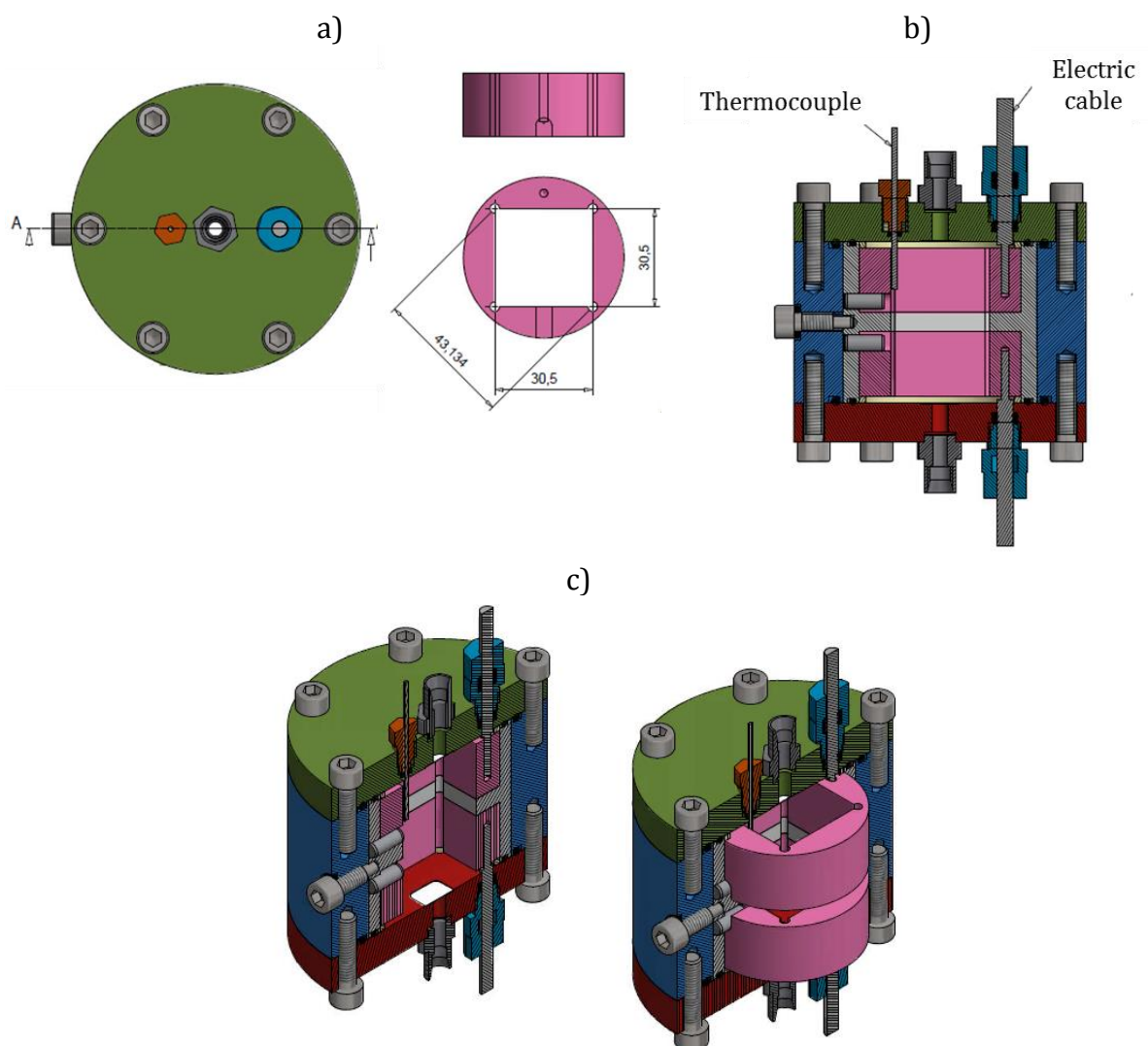


Figure 6.18. Column designed to test the 3D-printing honeycomb monolith: a) top view; b) internal front view; c) internal and external view.

The adsorbent with 15.612 g was packed in the column and was activated in situ under 0.250 SLPM helium flow rate at 373 K during 48 hours. After activation, the final mass of adsorbent was 14.076 g. Breakthrough curves were carried out at 298 K. The characteristics of the honeycomb monolith packed in the column are shown in Table 6.4. Single (CO_2) and binary (CO_2/N_2) breakthrough experiments were performed in this column in accordance with the experimental conditions given in Table 6.5.

Table 6.4. Characteristics of the 3D-printed honeycomb monolith adsorbent and adsorption bed used for the breakthrough experiments.

3D-printed honeycomb monolith adsorbent	
Dimensions (mm)	30×30×43
Dehydrated adsorbent mass (kg)	0.0141
Mass loss on activation (wt.%)	9.84
Bulk density (kg·m ⁻³)	923
Porosity	0.29
Adsorption bed	
Bed width (m)	0.0305
Bed height (m)	0.0305
Bed length (m)	0.0500
Thermocouple position (m)	0.02

Table 6.5. Operating conditions employed in the breakthrough curve experiments performed at with the 3D-printed honeycomb monolith (Ads, Des and Elec are an abbreviation for adsorption, desorption and electrification, respectively).

Exp	Initial condition	Flow rate ads/des (SLPM)	Ads feed comp (%)	Des feed comp (%)	P (bar)	Start time des (s)	Elec period (s)	Electric current (A)
1	He	0.288	He, 100		1.30	-	200 - 8500	19.8
2	He	0.260	CO ₂ , 24.4 He, 76.6	He, 100	1.30	5000	-	-
3	He	0.327	CO ₂ , 25.7 He, 74.3	He, 100	1.50	4000	4000 - 6200	19.8
4	N ₂	0.288	N ₂ , 100		1.30	-	200-3200	19.8
5	N ₂	0.248	CO ₂ , 23.0 N ₂ , 77.0	N ₂ , 100	1.30	3000	-	-
6	N ₂	0.246	CO ₂ , 23.2 N ₂ , 76.8	N ₂ , 100	1.40	3000	3000-5800	19.8

6.5.2 RESULTS

At the beginning of each experiment, the column is filled with He or N₂ at the feed temperature and pressure. The gas mixture was fed to the column until saturation. After this, the inlet stream was changed to helium or nitrogen and the desorption was started. The temperature in the middle of the column, the volumetric outlet flow rate and outlet composition were recorded.

Each breakthrough curve was simulated, and the experimental data were compared with simulations results. The software gProms was used to simulate the experimental data obtained, according to the information given in subsection 6.3 of Chapter 6.

The results of the breakthrough curves are given in Figure 6.19 to Figure 6.24. In these figures, graphic a) presents the molar fraction history of each component at the column outlet, graphic b) presents the total flow rate at the column outlet, graphic c) shows the temperature history at the middle position in the column. These graphics contain experimental data (points) and simulation results (lines). The transport parameters values required for the simulations are given in Table 6.6, and they were calculated at feed conditions using correlations as described previously, which were kept constant during the simulations. The linear driving force coefficients (k_{macro} and k_{micro}) were fitted for each experiment, as well as the heat transport parameters h_w and U .

Table 6.6. Transport parameters values used in the simulations of the breakthrough curves with the 3D-printed monolith.

Experiment	Exp.1	Exp.2	Exp.3	Exp.4	Exp.5	Exp.6
k_{macro} (s ⁻¹)	8.0	8.0	8.0	8.0	5.0	3.0
k_{micro} (s ⁻¹)	0.1	0.1	0.1	0.1	4.0	0.1
$D_{ax} \times 10^4$ (m ² ·s ⁻¹)	1.40	1.35	1.19	1.40	1.05	0.95
k_f (m·s ⁻¹)	0.017	0.016	0.010	0.017	0.011	0.002
h_f (W·m ⁻² ·K ⁻¹)	21.5	16.8	17.3	21.5	4.2	4.2

h_w (W·m ⁻² ·K ⁻¹)	85	10	3.5	23	2.5	0.5
U (W·m ⁻² ·K ⁻¹)	10	7	5	50	2	2
Voltage (V)	0.024	-	0.005	0.002	-	0.002

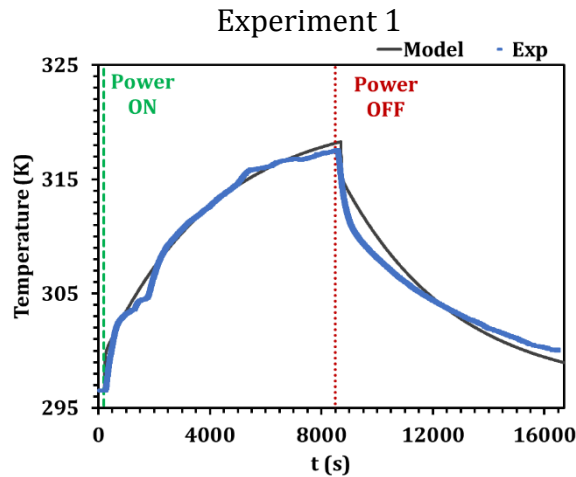


Figure 6.19. Results of experiment 1 with 3D-printed honeycomb monolith: temperature history at 0.02 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

Figure 6.19 presents the results of a heating experiment, in which the electrification of the column was done under a flow of helium. It is possible to observe that the 3D-printed honeycomb monolith needed a period of about 8000 s to increase its temperature up to about 320 K. Comparing this result with the ones obtained for the pellets reported in Chapter 5, the following should be pointed out. The pellets with the same amount of raw materials (30%AC-70%13X) did not increase the temperature when an electric current was applied. Therefore, it can be concluded that the material produced in honeycomb monolithic shape is better in terms of electrical conductivity than the pellets, for application is ESA processes. However, the reached temperature is below the pretended value, and the time required is too high. Also, the temperature reached is significantly lower than the one observed in the results with the honeycomb monolith with dimensions of 10×10×4 mm (section 6.2.6). One reason for the observed difference is that in the case of the smaller monoliths, the electrification is done by contact with two

alligators clips, while in the case of the packed monolith, the electrification is done by the contact of the square electrodes with the walls of the honeycomb monolith. But the most important difference, is the size of the monolith. The larger monolith has a much higher resistance, and the possible applied current (limit of the PSU) resulted in a low voltage, compromising the Joule effect. A current above this limit would be required to increase the temperature to feasible values in a material with this size.

In experiment 2, a single breakthrough curve with CO₂ was carried out. Figure 6.20 presents the results obtained.

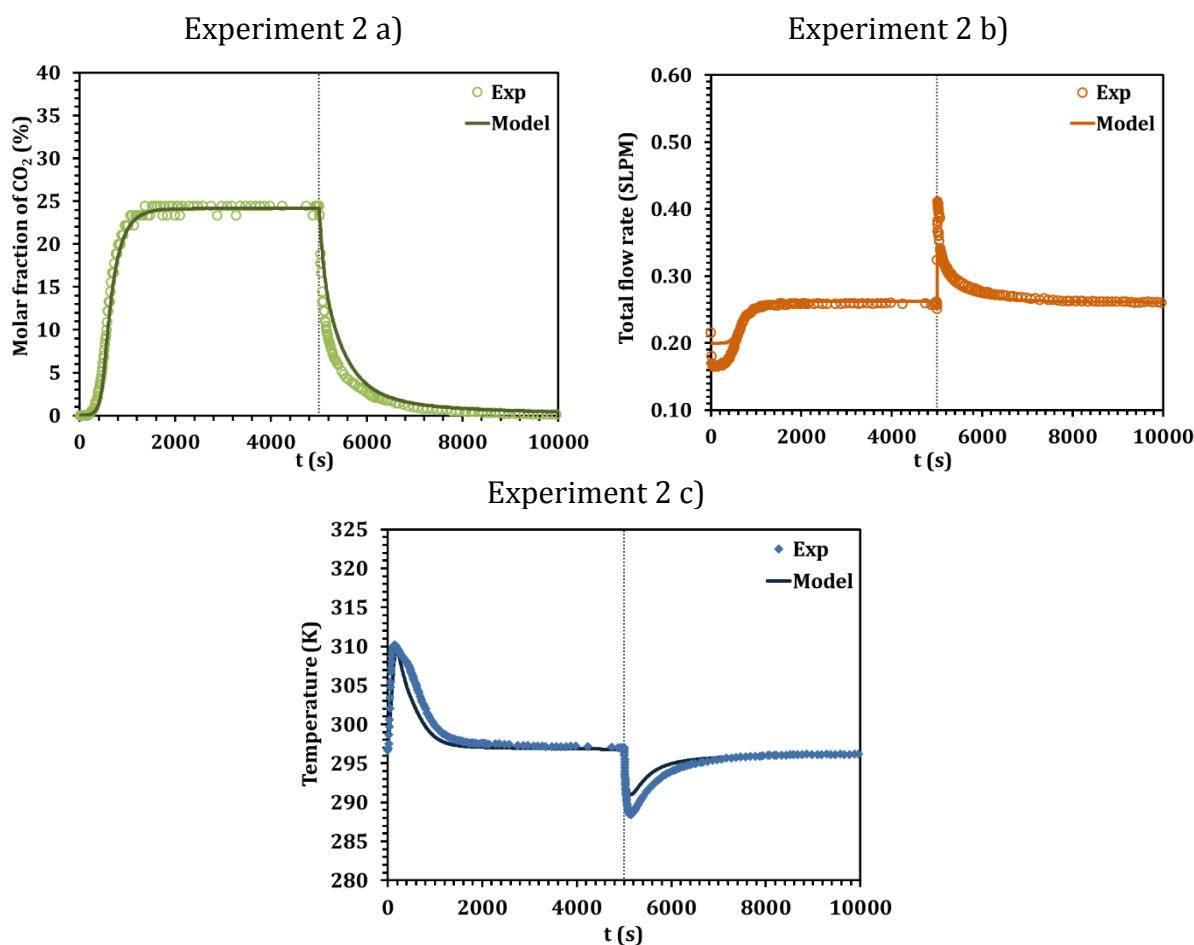


Figure 6.20. Breakthrough curve results of experiment 2 with the 3D-printed honeycomb monolith for inlet total pressure of 1.3 bar at 296.5 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.02 m (c). Points - experimental data; lines - model. Vertical dashed line - beginning of desorption.

The results obtained for the simulations are in agreement with the experimental data.

In experiment 3, a single CO₂ breakthrough was performed as in experiment 2, but in this case, the electrification was turned on during the desorption step (Figure 6.21).

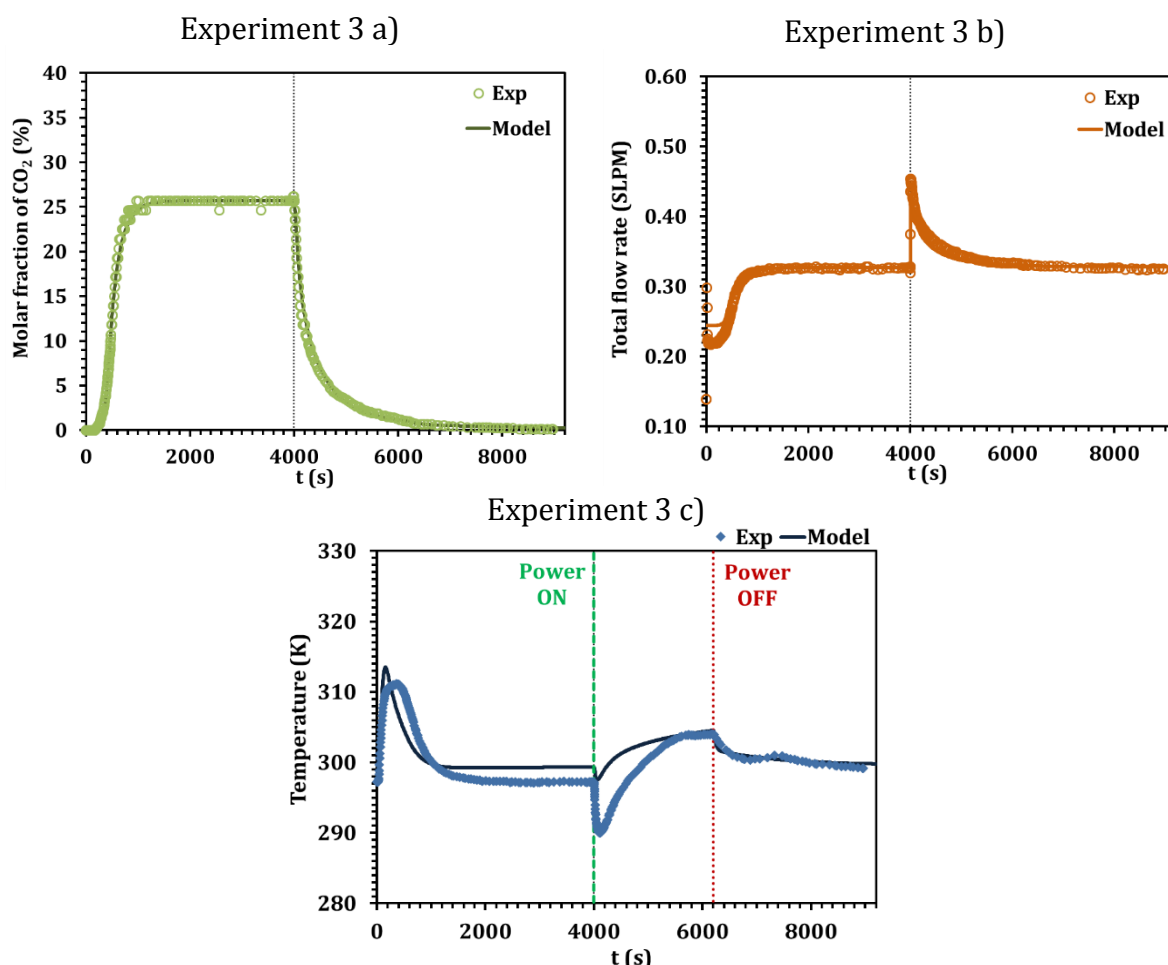


Figure 6.21. Breakthrough curve results of experiment 3 with the 3D-printed honeycomb monolith for inlet total pressure of 1.3 bar at 296 K: CO₂ molar fraction at the column outlet (a), total flow rate at the column outlet (b) and temperature history at 0.02 m (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

In this case, the simulation can also predict well the experimental results, except for temperature. Comparing the desorption step of this experience with the previous one, a decrease in temperature is observed in both experiments, but this decrease is not so pronounced in the second experience, as the endothermic effect of CO₂ desorption is balanced by the temperature increase due to the Joule effect. Indeed, a slightly higher temperature than the inlet temperature is obtained before the PSU unit is turned off. This temperature difference affects the time required to regenerate the bed. In experiment 2 this time is around 4000 s, while in experiment 3 it is around 3000 s.

Experiment 4 is a heating test, done with the column filled by nitrogen and under a nitrogen flow. The temperature history when an electric current is applied to the material in this experiment is shown in Figure 6.22.

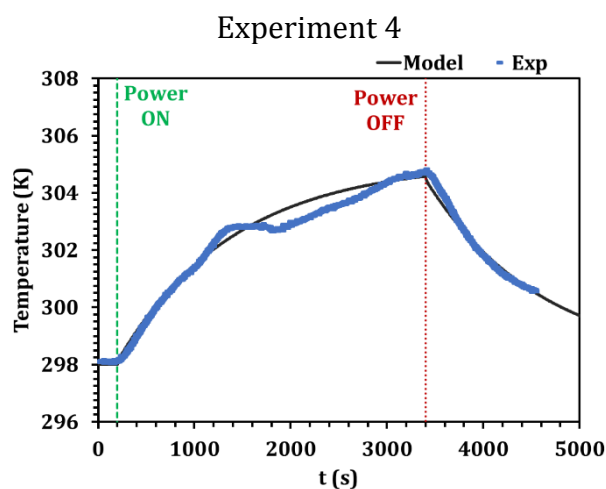
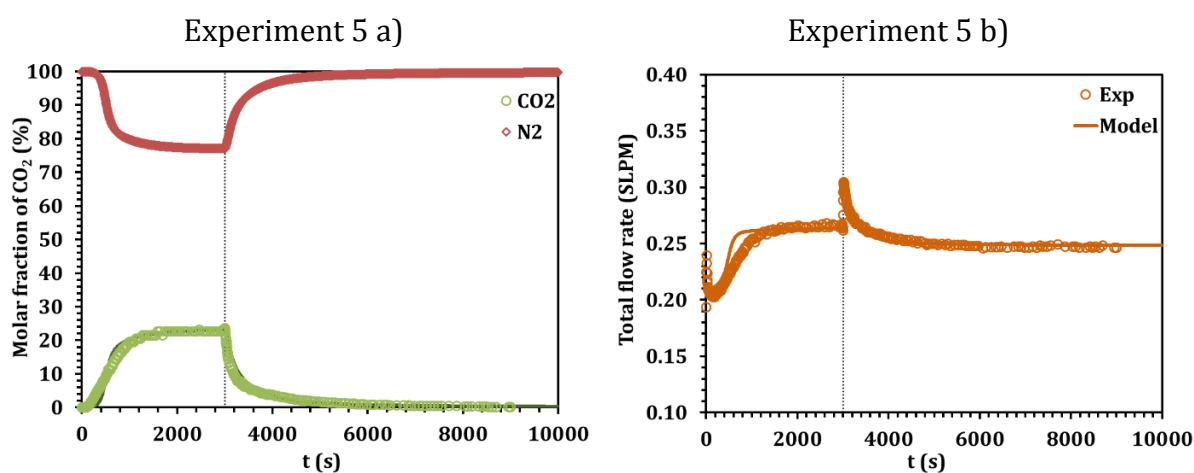


Figure 6.22. Results of experiment 4 with 3D-printed honeycomb monolith: temperature history at 0.02 m. Points - experimental data; lines - model. Vertical dashed lines – start (green) and end (red) of the electrification.

In this case, the temperature increase was only about 7 K.

Experiment 5 reports the results of a binary breakthrough curve with CO_2/N_2 (Figure 6.23).



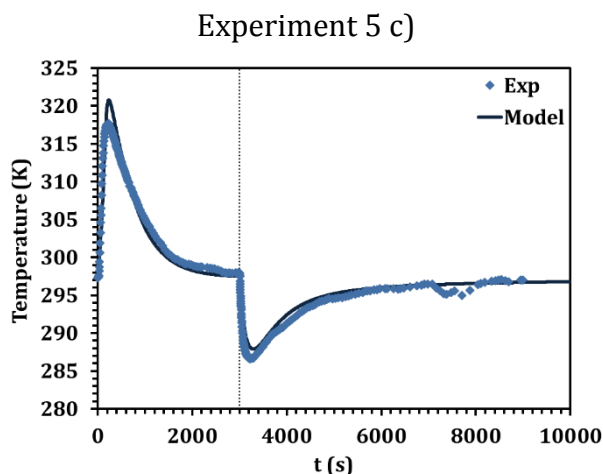
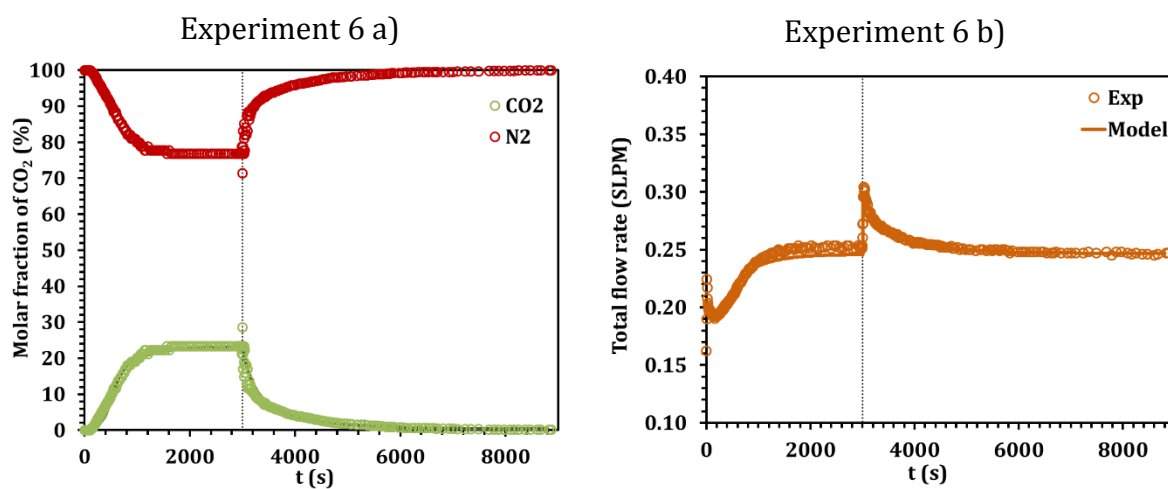


Figure 6.23. Breakthrough curve results of experiment 5 with 3D-printed honeycomb monolith for inlet total pressure of 1.45 bar at 298 K: CO_2 and N_2 molar flow rate at the column outlet (a), CO_2 and N_2 molar fraction at the column outlet (b) and total flow rate at the column outlet (c). Points - experimental data; lines - model. Vertical line - beginning of desorption.

In experiment 6, a binary CO_2/N_2 breakthrough curve was performed with electrification in the desorption step, and the results can be observed in Figure 6.24.



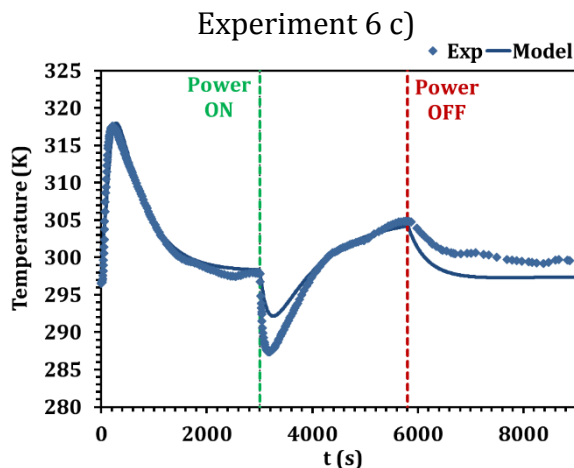


Figure 6.24. Breakthrough curve results of experiment 6 with 3D-printed honeycomb monolith for inlet total pressure of 1.45 bar at 298 K: CO₂ and N₂ molar flow rate at the column outlet (a), CO₂ and N₂ molar fraction at the column outlet (b) and total flow rate at the column outlet (c). Points - experimental data; lines - model. Vertical dashed lines – beginning of desorption/start of the electrification (green) and end (red) of the electrification.

In both cases, experiment 5 and 6, the simulations predict well the experimental results. Again, an increase above the inlet temperature is observed due to the Joule effect. However, the Joule effect is small due to the high resistance of the material.

6.6 CONCLUSIONS

In this chapter, the development of two honeycomb monoliths composed by 70% of zeolite 13X and 30% of activated carbon was presented. First, a wet mixture of raw materials, carboxymethylcellulose and water was done. The ink prepared was characterized by rotational and oscillatory tests using a rheometer. The experimental data obtained were well fitted by the Cross model, and a high zero-shear viscosity was estimated, 15701 Pa·s, demonstrating the high viscosity of the fluid. Viscoelastic behaviour of the paste, i.e., the stability and the strength of the microstructure was analysed by storage modulus and loss modulus measurements. The prepared ink was fed to the Discov3ry Extruder module of the Ultimaker 3D-printer, and the file of the designed honeycomb monolith was uploaded.

After the printing step, textural and mechanical characterization were carried out. The characterization demonstrated a high CO₂ capacity expected for this adsorbent, as well as the high mechanical stability.

The viability of this material to be applied in an Electric Swing Adsorption process was analysed by the heating tests with an electric current. The Joule effect in the material was observed when a constant voltage of 25 V was applied, and a current range between 0.05 and 0.13 A was needed to heat the smaller honeycomb monolithic material until 377 K in 180 s, approximately, representing a power consumption of about 3.25 W.

Pure CO₂ and N₂ adsorption equilibrium isotherms were performed at 303, 333 and 373 K. A value of 1.45 mol·kg⁻¹ at 0.09 bar and 303 K was obtained for CO₂, which can be considered an excellent result for CO₂ adsorption capacity.

A selectivity of 122.1 was estimated for this 3D-printed honeycomb monolith considering a mixture with 20% of CO₂ and 80% of N₂ at 1.5 bar and 298 K.

Breakthrough curves were performed using a bed packed with the 3D-printed honeycomb monolith. The modelling of the dynamic adsorption in a fixed bed was done and the results obtained a good prediction between experimental values and simulations.

3D-printed honeycomb monolith with dimensions of 30×30×43 mm demonstrated a poor heating when applied an electric current. The possible applied current according to the limit of the PSU used in the experimental set-up is not enough to address the resistance of the material.

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7 CONCLUSIONS AND FUTURE WORK

Electric Swing Adsorption process has been successfully implemented for purification of different streams. However, its application for carbon dioxide capture is still not sufficiently efficient to make this technology a competitive alternative to the current state of the art absorption processes. The main obstacle identified was the lack of an adsorbent material that combines good adsorption properties and electric properties needed for the Joule effect. The non-existence of commercial hybrid adsorbents with these two main properties, which are high CO₂ adsorption capacity and high electrical conductivity, was the core challenge of this work. The main goal of this work was the development of hybrid materials to be applied on Electric Swing Adsorption process for carbon dioxide capture from a flue gas stream.

The first task was the development of methods for adsorbent materials shaping in two different ways, namely extrudates and honeycomb monoliths. In LSRE-LCM laboratory, the research work lead to two successful methods for adsorbent materials shaping, which are extrusion (pellets/extrudates) and 3D-printing by Direct Ink Writing method (3D-printing honeycomb monolith). In parallel to the material being developed at LSRE-LCM, a cooperation with Tsinghua University in China was established, leading to the development of an extruded honeycomb monolith adsorbent composed by 70% of zeolite 13X and 30% of activated carbon. Therefore, within this work, three hybrid materials containing zeolite 13X and activated carbon as raw materials were produced and tested.

The extruded honeycomb monolith with dimensions of 50×50×50 mm was tested in terms of adsorption properties by single CO₂ and N₂ adsorption equilibrium isotherms measurements. The results demonstrated a CO₂ adsorption capacity of 1.33 mol·kg⁻¹ at 303 K and 0.10 bar, constituting a reduction of around 24% of the expected capacity considering the adsorbent composition in term of activated carbon and zeolite. Breakthrough experiments with different feed stream compositions were performed at 298 K and 2.4 bar and the experimental data were validated by a mathematical model adapted and applied to honeycomb monolith shaping. This model considered two solid diffusivity coefficients according to the micro and meso porosity observed in textural characterization. The simulations results demonstrated a good prediction of the experimental data. However, this extruded honeycomb monolith presented poor electrical conductivity and breakthrough experiments with electrification were not performed.

In order to improve CO₂ adsorption capacity and electrical conductive properties, pellets were produced by extrusion process with four different amounts of raw materials. An extensively characterization was done by diverse techniques, which demonstrated the viability of these materials. CO₂ and N₂ adsorption equilibrium isotherms were evaluated at three different temperatures. The results demonstrated that 30%AC-70%13X pellets have high CO₂ adsorption capacity, due to the higher quantity of zeolite present, followed by 50%AC-50%13X pellets, 70%AC-30%13X pellets and 100%AC pellets (from highest to lowest). At 303 K and 0.10 bar, the capacities are respectively 1.97, 1.50, 0.86 and 0.28 mol·kg⁻¹. In terms of electrical conductivity, the reverse sequence was verified, due to the decrease of activated carbon. The adsorption equilibrium data were accurately described by the Dual-Site Langmuir model in the studied temperature and pressure ranges. Breakthrough curve experiments of single (CO₂) and binary (CO₂/N₂) streams were performed, with and without electrification in the desorption step. A mathematical model was developed and employed to predict the experimental data. To study the viability of using these materials in ESA process, an ESA cycle containing four steps, feed, electrification, blowdown and purge, was simulated, using a fixed-bed with 0.03 m of diameter and 0.06 m of length, packed with 100%AC pellets in the first case study, and in the second case study, 50%AC-50%13X pellets were considered. The results with 100%AC pellets allowed to obtain a stream of CO₂ with 32.0% of purity and 29.2% of recovery. N₂ purity obtained in feed step is about 90.7%. In the second case study, i.e., using 50%AC-50%13X pellets, a stream with 63.7% of CO₂ purity, 43.3% of CO₂ recovery, and 93.4% of N₂ purity was obtained.

A hybrid honeycomb monolith adsorbent was developed using a recent technique in the gas separation area, which is 3D-printing technology. An ink with 70% of zeolite 13X and 30% of activated carbon was produced and the rheological measurements demonstrated the viability of this ink to be printed, due to the high viscosity of fluid, its viscoelastic properties and the stability and strength of the microstructure presented. Two 3D-printed honeycomb monoliths with dimensions of 30×30×43 mm and 30×28×10 mm were successfully printed. Electrical properties were evaluated by applying electric current in a piece of 3D-printed honeycomb monolith with 10×10×4 mm. The results demonstrated that 180 seconds were needed to increase temperature in 80 degrees, approximately, applying a constant voltage of 25 V, i.e., an energy consumption about 1 W·h.

Adsorption equilibrium isotherms of CO₂ (at 303, 318, 333 and 373 K) and N₂ (at 303, 333 and 373 K) were measured within a pressure range from 0 to 1.5 bar, using a gravimetric method. Once again, multicomponent Dual-Site Langmuir model was used to fit the experimental data. 3D-printed honeycomb monolith demonstrated a CO₂ adsorption capacity of 1.45 mol·kg⁻¹ at 0.10 bar and 303 K, which can be considered an excellent result, representing an increase of about 0.12 mol·kg⁻¹, when compared with CO₂ adsorption capacity of extruded honeycomb monolith with the same amount of raw materials. Comparing with the adsorption capacity of the 30%AC-70%13X pellets, a lower value is obtained, 1.45 vs 1.97 mol·kg⁻¹.

Single and binary breakthrough experiments were performed with and without electrification in the desorption step. The electrification of 3D-printed honeycomb monolith with dimensions of 30×30×43 mm demonstrated an increase of temperature about 20 K in 8000 s when helium is fed to the column at room temperature, revealing a poor heating of the material. The monolith used in the breakthrough experiments has a much higher length and electrical resistance. In this way the applied current (about 20 A, which is the limit of the power supply unit available) resulted in a low voltage (about 2 mV), compromising the Joule effect.

7.1 SUGGESTIONS FOR FUTURE WORK

After this research work, some of outlined objectives were executed successfully. However, some aspects are open for a future work.

In terms of Electric Swing Adsorption, it was verified that the main obstacle for the successful implementation of the process was the poor ability of the 3D-printed honeycomb monolith with 70% of zeolite 13X and 30% of activated carbon used in the breakthrough curves to heat. Considering the 3D-printed enhancements, it would be very interesting to create an ink with 50% of activated carbon and 50% of zeolite 13X to produce a new material, in order to improve the electrical conductivity.

The 3D-printing production could also be improved in terms of layer precision and thickness, which would result in materials with better finishing, i.e. more perfection. This would also allow the fabrication of honeycomb monoliths structures with a higher length. In addition, other binders or additives may be used to prepare the ink. The combination of adsorbent with good adsorption properties, such as zeolite 13X, zeolite 5A or a MOF, with other types of conductive materials, as polymers, such as polyaniline (PANI),

polypyrrole (PPY), polythiophene (PTP) or polyfuran (PFU), is a possibility. Recently, some works were published using Direct Ink Writing method to print inks with these polymers [1-3].

Another important obstacle that should be solved is the heating efficiency of the electrodes. According to the work reported by Rui Ribeiro [4], an electrification at higher electric power is more favourable energetically since the heating is faster and the energy losses are smaller. The main responsible for energy losses (at higher electric power employed) in the experimental setup tested are the electrodes. The design of the electrodes used could be reviewed, for example, develop electrodes with the same cylindrical shape, but adding a perforated base for gas passage and a high length, in order to improve the contact between electrodes and adsorbent.

Recently, a conductive graphene filament was created by Black Magic 3D and designed to print electrical conductive components using almost any commercially available desktop 3D printer [5]. A design of a rigid structure to insert in a honeycomb monolith produced using an adsorbent material with high CO₂ capacity, as zeolite 13X. This structure can be used as an “electrode” with a high length and high contact between the channels of the monolith and the conductive material.

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Appendix 1

At the beginning of this work, the first materials were produced by moulding process. This task of the work was important to define some parameters, such as, the amount of raw materials used to form a honeycomb monolith, the ratio between powders of each type of adsorbent, the adequate adsorbents and binders, and even more, the ratio between raw materials, binders and water amounts. During the experiments, the results were far from the final wanted material. In this was different approached were searched and followed.

This chapter assembles the main steps and important results obtained with the moulding process, because this was effectively the starting point of the work.

A.1.1 PRELIMINARY EXPERIMENTS

A large number of tests were developed. Different quantities of raw materials, binders and water were tested. Also, moulds fabricated with different materials were employed.

To summarize these tests, Table shows quantities of raw materials, binders and water used in ten experiments, denominated as M1 to M10.

Table A1.1.2 Composition of the pastes used for honeycomb monoliths production by moulding process.

Sample	Raw materials		Binders		Water (wt.%)
	13X (wt.%)	AC (wt.%)	CMC (wt.%)	Kaolin (wt.%)	
M1	71.7	21.6	1.1	5.6	38.6
M2	0	93.1	6.9	0	70.7
M3	48.1	46.5	5.4	0	67.8
M4	46.5	47.7	5.8	0	65.1
M5	48.1	46.5	5.4	0	67.8
M6	50.9	48.0	5.9	0	71.2
M7	50.9	48.0	5.9	0	71.2
M8	47.3	48.2	4.4	0	>70*
M9	46.6	48.7	4.7	0	65.5
M10	47.2	47.9	4.9	0	65.0

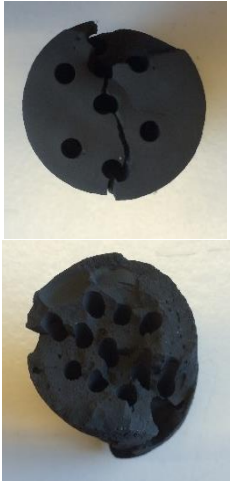
It should be noted that the first moulding experiment (M1) was only one that included kaolin in the mixture. The quantity of water used was only approximately 39%. The wet mixture was inserted in a designed mould made in stainless steel with sticks of the same material. It was possible to observe that after drying, the mixture glued to the walls of the tube and sticks.

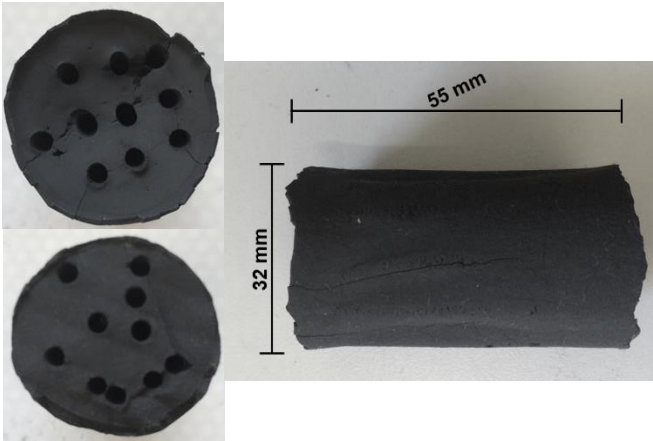
Experiment 2 (M2) was done with a mixture without zeolite, using only activated carbon and binder, to test the stiffness and the detachment of mould. In experiments M3 to M10, there were slight variations between the amounts of powders. The main purpose of these tests was the evaluation of the demoulding behaviour of the different materials used to built the mould, as indicated in the experimental scheme presented in section 3.2 of Chapter 3.

Table A1.1.2 summarizes the main characteristics of the prepared materials and observations of these experiments.

Table A1.12. Figures and characteristics of some materials produced by moulding process.

Exp	Mould	Electrical Resistance	Parallel channels	Dimensions (d×l, mm)	Observations	Results
M1	Stainless steel	No	10	21 × 100	High rigidity verified; No demoulding because materials sticks to the mould;; Large number of holes (evaporation of water).	
M2	Glass	130 Ω	4	31 × 35	High rigidity verified; Some defects in material; Channels demoulding was not good.	
M3	Glass Teflon	1250 Ω	No	45 × 10	High rigidity verified; Some defects verified; Body demoulding of the glass beaker and teflon beaker was good.	
M4	Glass (with resin)	1550 Ω	No	45 × 10	High rigidity verified; Small defects; Body demoulding was good.	

Exp	Mould	Electrical Resistance	Parallel channels	Dimensions (d×l, mm)	Observations	Results
M5	Teflon; Stainless	1100 Ω	6	39 × 15	High rigidity, but cracked when sticks were removed.	
M6	Teflon; Stainless steel involved in filter paper	980 Ω	8	29 × 20	High rigidity verified; Large number of holes verified; Difficult to remove the sticks.	
M7	Teflon; Wood	650 Ω	12	29 × 20	High rigidity verified; Large number of holes verified; Some difficult to remove the sticks.	
M8	Teflon	3300 Ω	7	29 × 30	Medium rigidity verified; Teflon sticks easily removed; cracked in the demoulding step.	

Exp	Mould	Electrical resistance	Parallel channels	Dimensions (d×l, mm)	Observations	Results
M9	Teflon	400 kΩ	16	31 × 23	Demoulding of mould and sticks was very good; Few defects observed.	
M10	Teflon	170 Ω	10	32 × 55	Demoulding of mould and sticks were very good; Few defects observed; Channels are not aligned nor parallel along the monolith.	

The best result obtained was the material produced in experiment M10. A piece of honeycomb monolith with 32 mm of diameter and 55 mm of length was developed.

A.1.2 ADSORPTION EQUILIBRIUM ISOTHERMS

In order to understand the feasibility of this monolith and the quantities of raw materials, binders and water used, adsorption properties of the material, especially the CO₂ and N₂ adsorption equilibrium capacity was measured by adsorption equilibrium isotherms at three different temperatures.

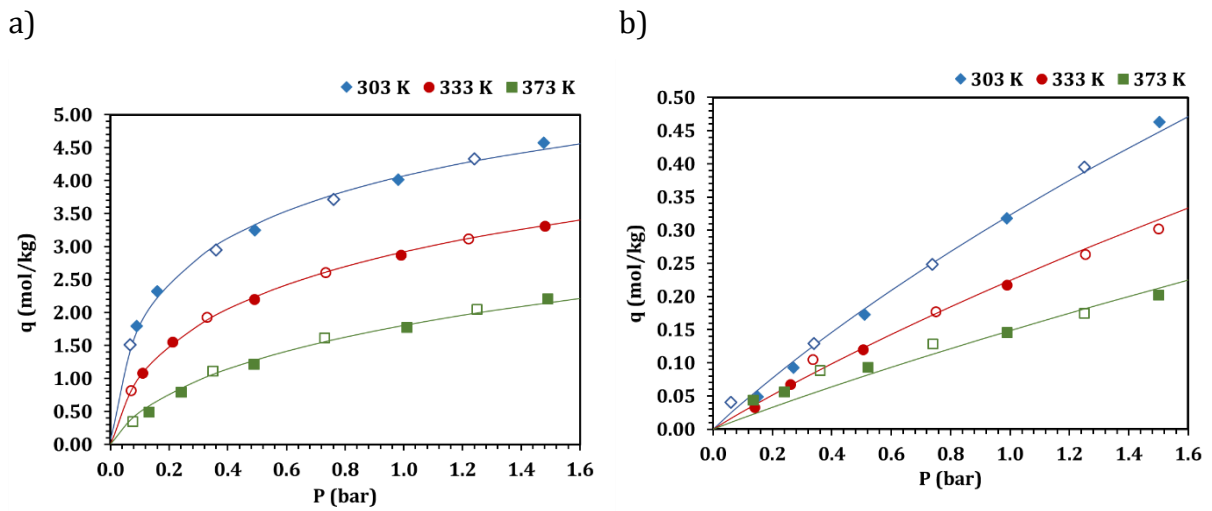


Figure A1.1.1. Adsorption equilibrium isotherms of a) CO₂ and b) N₂ on the honeycomb monolith developed by moulding process (M10): experimental points (closed adsorption, open desorption) at 303 K (◆), 333 K (●), 373 K (■) and (—) the Toth model isotherm fitting.

The experimental data were fitted with the Toth isotherm model, represented by equation A1.1.1:

$$q_i = q_{m,i} \frac{K_i P}{[1 + (K_i P)^{n_i}]^{\frac{1}{n_i}}} \quad \text{A1.1.1}$$

The fitted parameters, q_m , K_i^0 , n_i and $(-\Delta H)$ were obtained by minimizing the sum of absolute errors between calculated and experimental values with the Excel Solver add-in. The parameters obtained are given in Table A1.2.1.

Table A1.2.1. Fitting parameters of the Toth model for CO₂ adsorption equilibrium on monolith produced by moulding process (M10).

Material	Species	q_m (mol·kg ⁻¹)	K_i^0 (bar ⁻¹)	n_i	$(-\Delta H)$ (J·mol ⁻¹)
Monolith by moulding (M10)	CO ₂	8.82	7.71×10^{-5}	0.38	31074
	N ₂	4.85	7.44×10^{-4}	0.65	12066

It is possible to observe a good fitting obtained between experimental data and Toth isotherm model in Figure A1.1.1.