



Treball Final de Grau

Computational simulation of CO₂ capture onto Mg-MOF-74 from industrial gas streams with impurities

Simulació computacional de la captura del CO₂ provinent dels gasos de post-combustió industrials en la Mg-MOF-74

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La paciència és la mare de la ciència

Dita popular

Quan algú comença a escriure uns agraïments, ha de ser conscient per endavant que seran incomplets. En aquest cas encara amb més motius, doncs al tractar-se de l'àmbit científic, no es poden contar totes les persones que indirectament han fet possible que jo realitzés aquest treball. Ortega i Gasset diu a la *Rebel·lió de les Masses*, que en dividir-se la ciència de manera inevitable en sectors cada vegada més concrets i especialitzats, el científic, corre el risc d'oblidar l'ampli ventall de camps en que s'originen les bases fonamentals de les seves investigacions. En paraules textuais exposa: " Pero si el especialista desconoce la fisiología interna de la ciencias que cultiva, mucho más radicalmente ignora las condiciones históricas de su perduración, es decir, cómo tienen que estar organizados la sociedad y el corazón del hombre para que pueda seguir habiendo investigadores". Així al meu entendre, els descobriments que puguem fer com a investigadors no són "nostres", o almenys no només nostres, sinó que pertanyen a cada petit esglaó que milers de mans han construït al llarg de la història fins arribar al punt final, i es dilueixen en el mar de vessants i formes a les que s'estén el mètode científic. Per tan, el primer paràgraf d'aquests agraïments vol recordar a totes aquelles persones que han posat les bases per a la realització d'aquest treball, i en definitiva, a tota la gent que fa ciència per amor a l'art.

El segon paràgraf és per les dues persones que han col·laborat de la manera més activa i directa en aquest treball. Vull agrair als meus tutors, el Dr. Xavier Giménez Font i el Dr. Daniel Bahamon García, les hores dedicades i els consells que m'han brindat il·limitadament. Però molt per sobre d'això, que m'hagin sabut transmetre la passió per la investigació. Cada reunió per analitzar els resultats ha esdevingut per a mi una classe magistral d'un valor impagable.

Per últim vull aprofitar per agrair als meus pares tot el que han fet per mi sempre. Per a ells és aquest treball. Per a ells i pel meu germà, amb qui més paraules són sobreres.

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SUMMARY

In this assignment, molecular simulations by means of grand canonical MonteCarlo (GCMC) techniques, are used in order to study the CO₂ adsorption process in the Mg-MOF-74, a new generation adsorbent material.

The application of this material is designed (in order to be situated as a final element) for the CO₂ capture present in post-combustion industrial gases streams, in order to avoid the emission of this gas towards the atmosphere. For this reason it has been studied as well the behavior of the Mg-MOF-74 towards other current species in these gases such as N₂, NO₂, NO, O₂ and SO₂, since they are potential competitors to be integrated in the adsorption centers of the MOF and they can affect the global yield of the process.

In addition, different desorption processes have been evaluated in order to regenerate the adsorbent material, taking into account their energetic cost index.

Keywords: CO₂ capture, adsorption, MOFs, impurities

RESUM

En aquest treball s'utilitzen simulacions del gran canònic de MonteCarlo (GCMC) per tal d'estudiar el procés d'adsorció del CO₂ en la Mg-MOF-74, un material adsorbent d'última generació.

L'aplicació d'aquest material està dissenyada (per situar-se com un element final) per a la captura del CO₂ present en les corrents de gasos de post-combustió industrials, per tal d'evitar l'emissió d'aquest gas a l'atmosfera. Per aquest motiu també s'ha estudiat el comportament de la Mg-MOF-74 en vers altres espècies presents en aquests gasos com l'N₂, l'NO₂, l'NO, l'O₂ i l'SO₂, ja que són potencials competidors per integrar-se als centres d'adsorció de la MOF i poden afectar al rendiment global del procés respecte al CO₂.

A més s'han avaluat diferents processos de desorció, per a regenerar el material adsorbent, en funció del seu índex energètic.

Paraules clau: Captura de CO₂, adsorció, MOFs, impureses

1. INTRODUCTION

In the era of technological and scientific developments, the unstoppable consumerism and the consumption excesses have become embedded in the basis of our society and, in name of progress, they have risen up themselves as the pillars that govern the dynamics of our days.

It has been a while since we first noticed the effects of these behaviors and, as the late studies suggest, they will become more intense in the following years.

In this crossroad that the history has set apart for us, mankind must decide whether it is going to take responsibility for its actions and will claw back the wheel of its destiny or, instead of that, it is going to remain unconsciously drifting, ignoring the warnings of the earth and ignoring, whatever they are, all the consequences that this decision will carry.

In this sense, each individual beholds the moral duty to take charge of his acts and, as far as possible, to walk towards a sustainable future.

Furthermore, in the same way, the scientific community must approach its studies towards the resolution of these problems, which come attached to the possibilities that science has opened itself to society and that has been incapable of managing.

It is the scientific community that bears the burden of finding out solutions, because it is the one that has got the tools and the knowledge required to achieve it. So, as it holds the might, it also holds, in an inseparable way, the responsibility.

The first step then, in order to solve these problems, is to detect them and be aware of them. Following this reasoning it emerged, in the seventies, a series of conferences dedicated to warn the political class. These conferences included the first evidences of the dramatic results of the exacerbated consumerism.

The first international conference relating to environment took place in Stockholm in 1972. The path that opened it had its continuation 20 years later, in Rio de Janeiro 1992, known as the Earth Summit, even though the official denomination is still The United Nations Conference on

Environment and Development, UNCED. The next one conference also took place in Rio, in 2012, and it is called Rio+20, in response of the ONU call to convoke the fifth Earth Summit.

As a result of these conferences, in 1997 it was signed the Kyoto protocol, which is the first binding treaty in matters of reduction of greenhouse gas emissions, and was agreed by 184 countries of the ONU. Recently, to update the levels of emissions that were established in Kyoto, there took place the so called Paris Agreement in 2015. This time the agreement was ratified by 195 countries and will begin to be applied after 2020.

One of the points where all these conferences and treaties come across is the imperious necessity of reducing the CO₂ emissions to the atmosphere, given that it is one of the gases that contribute more to the greenhouse effect, and by extent, to the global warming.

From this amalgam of reasonings and contextualizations comes this work. The aim of this work is to be nothing more (and nothing less) than a small grain of sand in the investigation of new techniques to reduce the emissions CO₂ in the atmosphere.

As it commonly happens in the scientific area, the great discoveries and contributions have been always linked to the needs and demands of the society. Among the different methods reported in the literature for CO₂ capture, adsorption has been gaining special attention, and the methods to adsorb have widened a great number of fronts of investigation during the last thirty years. These new techniques aspire to be a better alternative to the classic systems that have been used until now, and from them it is expected to obtain higher performances in the capacity of adsorption of carbon dioxide that is present in the flows of the combustion gases of the industries.

These studies are basically focused on the research of new materials, more efficient and more selective. The two big families that are having really promising results are the zeolites and the MOFs (Metal Organic Frameworks). It is about porous solids to integrate inside the CO₂ molecules.

In this work, the behavior of a specific MOF: the Mg-MOF-74 is studied. The MOFs are molecules "à la carte", which means, molecules designed and synthesized specifically to carry out, in the best way possible, the task in which we are interested.

The special feature of this MOF composed of organic solid with metallic centers (Mg in this case), is that its spatial disposition and distribution of electric charges can allow, extraordinarily well, the coupling of CO₂ molecules.

In parallel to the chemical engineering, the chemical-physical or materials engineering fields, there is another field that has significantly progressed, and is holding a huge importance, due to the complexity and the calculus potency that it offers is the computing, and more precisely, the computational simulation.

During the last years, there have been devised digital computers that are able to simulate interactions between particles. In order to carry through it, in addition to the necessary information that they have got integrated, such as the distance between atoms and its distribution in 3D, or the electric charge and attraction and repulsion forces that happen between each pair of concrete atoms, they help themselves with theories emerged from fields such as the deterministic physics, like the Molecular Dynamics, or the probabilistic physics, as in the great canonic MonteCarlo's case.

The power of big computers, which are capable to work with digits that supposed an impenetrable barrier, and it's incredibly high calculus speed, that increases by a factor of 2 each year and a half, make it possible for the new softwares that are being develop to be able to keep working taking into account higher numbers of particles, to the point that are capable to represent simulations more accurate and closer to the reality.

This fact has carried a so huge change in the investigation paradigm, that, by now, it represents a third work methodology, alternative to the two classical ways to work in science, the theoretical and the experimental.

Obviously, these three methodologies do not exclude one each other, but complement each other and supplement the deficiencies of the other. For the topic that is being treated here, the computational simulation is the one that offers more advantages, and the one that is actually being used more. This is due to the fact that allows us to deal with the large spectrum of materials that there exist, and the infinite combinations of percentages and kinds of impurities that occur in the industrial gases of post-combustion in a more direct and less expensive way, while reducing the required time and bringing physical meaning of the adsorption behavior. The possibilities are so many that they could not be carried to all the levels of the lab, and the computational simulation offers the opportunity to do an exhaustive selection of the MOFs. The ones that overcome this screening will go later through other levels of selection.

2. OBJECTIVES

The main goal of this study is to go forward in the comprehension of the adsorption process of CO₂ in the Mg-MOF-74, to certain levels and real percentages that appear in the industrial gases of post-combustion, and how is the behavior with certain impurities in the flue gas

In order to achieve so, more concrete objectives have been established.

Perform pure adsorption isotherms for the main components such as CO₂, N₂, among others, on Mg-MOF-74, in order to validate the simulation with experimental data that appear in the bibliography and recent studies.

Evaluate pure component adsorption of impurities molecules of interest, such as NO, NO₂ and SO₂. In this way, it is pretended to evaluate if the MOF studied has more affinity to adsorb these contaminants above CO₂.

Perform a parameterization of the adsorption the isotherms for all the elements.

Perform simulation with mixtures and percentages of impurities extracted from the compositions of flue gases, at working conditions of real industrial processes.

Evaluate the feasibility of using different systems of recuperation of the adsorbent to this type of separation, in terms of performance and energetic costs.

3. FUNDAMENTALS

The following chapter is a general review of the theoretical basis in which the adsorption process is based.

3.1 Adsorption

Adsorption is a separation process of one or more components from a mix in liquid or gaseous phase through a solid adsorbent of different kinds. During this process one or more species are accumulated, either atoms, ions or molecules, in a certain interim surface.

Due to its characteristics, adsorption is one of the most relevant unitary operations in the reduction of polluting gases, since its great selective capacity allows capturing the species of interest and to control the emissions towards the environment.

The quantity of accumulated matter is directly linked to the dynamic equilibrium between the adsorbent and the adsorbate, understanding the adsorbent as the solid where it is retained the transferable component of the fluid phase and the adsorbate as the befitting component of the fluid phase retained on the adsorbent surface. The equilibrium depends on the properties of the adsorbent and the adsorbate, in other words, on the capacity of adsorption of the adsorbent and on the way in which the two species involved interact. In order to carry out the adsorption, the use of an external force is not required, since it happens in a natural manner. It is a spontaneous process, in which a reduction of both the free energy (ΔG) and the entropy (ΔS) of the system is produced, assuming, of course, that the adsorbent is not saturated.

Furthermore, this dynamic equilibrium also depends on the conditions in which the process is executed, and therefore, the modification in the pressure and in the temperature affects in a determinant way the global results. In the same way, if the conditions vary once the adsorption has been produced, desorption can be produced, which means the inverse process. This fact offers the essential possibility to retrieve the adsorbent when the separation has been produced, so that it can be utilized again, either by increasing the temperature or reducing the pressure. These possibilities are treated in deep later, in the section of the adsorption applied to the CO₂.

However, desorption does not always appear in a complete form, since it also depends on the type of forces interacting between the adsorbent and the substrate, and on the bonds that have been produced. Generally, the adsorbent disposes of pores that act as active centers and can accept new molecules to get in contact with them. The nature of these new created interactions will determine, in a very important measure, the possibility or not to desorb. Also, due to its nature it can be distinguished two different types of adsorption: the chemical adsorption and the physical adsorption.

The physical adsorption or physisorption is characterized by the creation of feeble bonds that are produced due to forces of van der Waals and dipolar forces. In this way, the adsorbed species do not alter the molecular orbital and, therefore, they are not fixed in a specific place on the surface, but they move freely through the interphase, occupying the different active centers vacant, attracted by the permanent action of the dipoles and the induced dipoles. Thus, due to their nature, physisorption prevail in low temperatures, and it is an exothermic process.

On the other hand, the chemical adsorption or chemisorption appears when there is an intersection of chemical type between adsorbent and adsorbate. In other words, it appears when there is an electron sharing or exchange between the involved elements. These types of interactive forces, which can either be ionic or covalent, are very strong, and the bonds of electrons, between gas and liquid in the active centers, provoke a reordering of the molecular orbital.

These differences lead to different conducts in the disposition of the adsorbate in the interphase, in the adsorption speed and other aspects described below.

- **Physical adsorption:** Produced rapidly, is able to create more than a layer of adsorbate (multilayer). It decreases with temperature, it is not specific and does not lead to dissociation of adsorbed molecules. Therefore, it has reversible character and there can appear desorption if the system conditions vary.
- **Chemical adsorption:** Slower than the physical, as it has to surpass the activation energy in order to break the bonds, and therefore, it increases with temperature. Because it generates strong chemical bonds, it can only create one adsorbed layer. It has a much more specific character due to the reactions that must occur between the fluid molecules and the active centers of the adsorbent, and dissociation of molecules often happens. Due to all these facts, it is usually irreversible, and it is very difficult that desorption is produced.

3.2 Thermodynamic and adsorption isotherms

The most common way to represent than adsorption process is by the adsorption isotherm. Adsorption isotherms are plots in which it is depicted the quantity of adsorbed material by the adsorbent in the equilibrium, either by grams or by adsorbent volume, in relation of the relating pressure and at a certain temperature. Thus, it can be illustrated in a clear way how the changes in pressure affect the results obtained from adsorption capacities.

Furthermore, from their form, it can be extracted essential information about how the nature of the adsorption changes to different pressures, which are the interactions between the species involved or which is the distribution of the porous in the interphase of the material. Therefore, from them, it is possible to enlighten which are the fundamental intern processes that occur. Isotherms are currently classified in six different types, five of them were proposed by Brunauer, Deming and Teller in 1940 [1], and the last one has been incorporated during the last years. Depending on the process that they describe, they adopt different forms, which are illustrated below.

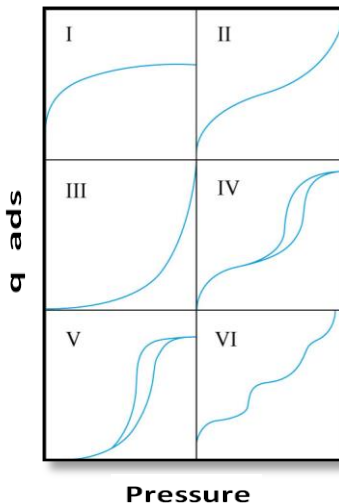


Figure 1. Adsorption isotherms types

In order to be able to understand the six types of isotherms, it is necessary to acquire previous knowledge about the different kind of porous materials that exist, since these affect directly the form of isotherms.

According to IUPAC [2], there are three different types:

In first place there are the macroporous, with pores of more than 50 nm of diameter. They do not have an elevated specific surface, thereby they are usually used as a support of materials with smaller pores, since when they allow the passing of gas flows to others, they improve its performance.

Secondly there are the mesoporous, with pores between 2 and 50 nm. They possess a large interior surface, and that is why, compared with the microporous, they are suitable to adsorb large molecules.

Finally there are the microporous, with a diameter of less than 2 nm. They are suitable to adsorb small molecules, and they are the most used in separation and catalysis. The most commons are the inorganic materials and the activated carbons. The fundamental reason why different types of isotherms are produced according to the nature of the adsorbent, is that in the mesoporous solids, the adsorption appears at medium or high relative pressures, while in microporous the covering of the pores is produced at low pressures.

Therefore, the first isotherm of the figure above is characteristic of processes in which the nature of the adsorbent is microporous. In it, it can be observed a fast improve of the quantity of gas adsorbed at low relative pressures, and at high pressures it tends to a maximum in the quantity of the adsorbed mass. This is due to the fact that micropores are already full and cannot accept more molecules in their structure, from which it can be realized that there is only one monolayer of adsorption. Due to its characteristics it is also called Langmuir isotherm. This shape is really common in active carbons and in zeolites.

In the type II isotherm, the quantity adsorbed increases in a relevant way in two steps. It firstly increases up to a certain limit, but suddenly it considerably increases again. This is because a multilayer adsorption is produced. The first saturation point indicates that it has been completed the first layer of adsorption and then it begins the adsorption of the following layer. This isotherm is typical of the macroporous materials.

The third isotherm is also typical of the macroporous solids, but it holds a peculiarity which makes it rather complex. The affinity between adsorbent and adsorbate is very weak. This provokes that at low pressures the adsorption is not nearly produced, but at higher pressures the interactions are much stronger inside the pore, and this fact gives driving force to the process and it allows the adsorption.

The type IV isotherm occurs in materials with mesopores like alumina and silica. Its main property is the presence of hysteresis cycles. It is similar to the type II isotherm, although at medium pressures it occurs the capillary condensation phenomenon in the mesopores. This phenomenon produces a stream of desorption in the global process that explains the hysteresis loop.

The type V isotherm is one of the least commons. It could be understood as a mixture between the properties of the type III and type IV isotherms. The affinity between the adsorbent and the fluid is low, and the hysteresis cycle links the fulfilling of mesopores and the capillary condensation. An example of this phenomenon is the water vapor adsorption by active carbons at temperatures close to the environment.

The last isotherm, type VI, represents the adsorption processes that appear in a stepped way. It is an adsorption in a cooperative multilayer, which means that each step contributes in a positive manner to the formation of the next layer throughout lateral interactions between molecules. Even though it is not a common adsorption, it can be produced in adsorption processes of noble gases in quite uniform surfaces.

3.3 Parameters/ Indicators of the separation process

There exist different parameters to evaluate the advantages, in terms of affinity, capacity and regeneration, of an adsorption process with respect to another one which is in different conditions or that works with another adsorbent. One of the most important ones at equilibrium conditions are the isosteric heat of adsorption, the selectivity and the working capacity.

It must be mentioned that in the process there also intervene concepts related to the kinetics of mass transfer. And in some cases they have special relevance, as the kinetics control the timing of each cycle during the adsorption processes (usually, the controlling phase of the process is the intern diffusion).

3.3.1 Heat of adsorption

The heat of adsorption, also known as isosteric heat, is a measure of the force of attractions between the adsorbent specie and the adsorbate. It gives information about the quantity of energy that is lost (dissipated) during the adsorption process, since a gas molecule reduces its potential energy when it contacts a surface with adsorbent capacities. It represents one of the

most important thermodynamic indicators in order to understand the temperature effects and the implications that it entails when desorption or regeneration occurs.

In this way, isosteric heat, q_{st} , is defined as the necessary heat that must be applied to the system in order to extract an adsorbed molecule. If the isosteric heat is very high, it implies that it will be very difficult to desorb. However, on the other hand, if it is really low, it means that the yield of the adsorption process will be low as well, and a practical adsorption will not be able to be produced. Then, it is necessary to reach a commitment in which the adsorption is produced in an efficient manner and, at the same time, to obtain a high regeneration.

The isosteric heat is computed with the equilibrium between both phases that are involved in the process: the condensed phase and the gas phase. Thereby, applying the appropriate simplifications, it can be reduced to Clapeyron equation:

$$Q_{isost} = -R \left. \frac{\partial \ln P}{\partial (1/T)} \right]_N = RT^2 \left. \frac{\partial \ln P}{\partial T} \right]_N$$

The Clapeyron equation allows calculating the slope of the equilibrium line dP/dT , at any value of P and T . Hence, it is independent of these two parameters and it only depends on the nature and the interaction between the two participant species.

Besides all the uses explained so far, the value of the isosteric heat can also help to distinguish the physical and chemical adsorption processes: in physical adsorption the isosteric heat achieve values between 20 and 70 kJ/mol, and as chemical adsorption the processes reaches values above 80kJ/mol [3].

3.3.2 Selectivity

Selectivity is a concept that allows evaluating in which measure one species is adsorbed in relation to other ones.

Hence, it is based on the differences of affinity that exist between the adsorbent and the rest of involved species.

Thus, information can be collected regarding which are the molecules preferentially adsorbed in the studied adsorbent, and which mixtures will lead to good or bad yields in the adsorption of the molecule of interest.

Mathematically, selectivity is expressed as the quotient between the adsorption capacity of a component and the corresponding capacity of another component in a given mixture.

$$S_{12} = \frac{x_1/y_1}{x_2/y_2}$$

Where x and y denotes molar fraction in adsorbed and fluid phase, respectively.

3.3.3 Working Capacity

This parameter is defined as the difference between the quantity adsorbed of a certain substance and the quantity that will remain in the adsorbent after regeneration.

$$WC (\Delta q) = q_{ads} - q_{des}$$

The quantity adsorbed is the maximum quantity of the adsorbate which the adsorbent material is capable to accept at determined conditions. Once the regeneration is produced, it is really hard and expensive to desorb the 100% of the adsorbed quantity. So, regeneration is produced in some conditions of P and T, reaching a commitment between desorption yield and energetic cost.

Hence, when working on a typical industrial cycle in which the adsorbent surface is reutilized, the maximum adsorption that can be reached during the first cycle cannot be used as a calculus value, but it has to be used the value of working capacity, which is the adsorption capacity that the adsorbent will keep during all the cycles when the process reaches a stationary state.

3.4 Considerations and specific technologies for the adsorption of CO₂

The need to apply adsorption to a very concrete element, the CO₂, has lead to the evolution of the research of new adsorbents towards very concrete paths, in order to find the right and specific material for the adsorption of CO₂. Moreover, the gases mixtures, which can produce competences in the adsorption, are also established by the species that normally go along with this gas inside the industrial post combustion flows. Therefore, the adsorbent must be selective towards carbon dioxide, facing some concrete competitors, and must have the maximum level

of working capacity in similar pressures and temperatures conditions such the ones that appear in the industrial gases.

Apart from the implications at small scale of each minuscule element that affects adsorption, and that it can be determinant in the consecution of new goals by itself, we must be aware that, in practice, the models must be implanted at industrial scale, to be able to deal with the huge quantities of carbon dioxide that the human activity produces daily.

This part is not a trivial topic; there are lots of possible options and, at so high work volumes, each detail contributes in a decisive way in economical aspects and in the yields. Therefore, it must be found the best option in each case among a so large spectrum of possibilities that does not envy, in quantitative terms, the number of stars of our sky.

Once the CO₂ is separated successfully, it must be given a utility. There are many applications of the CO₂, especially as a raw matter in the chemical industry.

In this headland, the ideas exposed above are deepened, in order to get a global idea of the adsorption process of CO₂ in the present, as well as the paths foreseen to be walked through in the future.

3.5 CO₂ capture methods

Nowadays several methods are used in order to capture the carbon dioxide molecules, which can be differentiated by the strategies used to carry out the separation. Whether if they are of chemical or physical nature separations, or by its origin and features of the used materials. The most important ones are explained below.

- **Cryogenic separation:** It is based on the differences in the boiling points of the participant gases. Although theoretically it could be an alternative for the CO₂ separation, this process requires, in order to reaching the necessary conditions, a so elevated energy demand (high pressures and very low temperatures) that, in practice, it is not a reasonable option. Moreover, if the mixture has water presence, it must be separated previously in order to not be solidified during the process.
- **Biological separation (microbes and algae):** Algae are capable to capture the CO₂, since they use it to carry out the photosynthesis process. This property allows the development of photo bioreactors that, from residual waters and

existent CO₂ in the post combustion gases, can produce microscopic algae which can be used as a biofuel.

However, the disadvantages of this technique are many: the slowness of the generating algae process, the necessity of a continued water supply with a high DBO content, the need of solar light which means that the process must happen in the open air, with possible polluting agents and variations of temperatures, or in a closed enclosure, limiting the evaporation and increasing expenses. The main advantage it holds is the transport and storage of CO₂ thrift, since algae are re-utilized as fuel in the industrial plants. However, currently, the obstacles are too many and a very important development is required for this technology to be able to compete with the rest.

- **Absorption:** Absorption (solvent scrubbing) is one of the most established and used methods currently in the chemical and oil industry. It is divided in physical absorption, where it is favored the process at high pressures and low temperatures, since it follows the Henry law, and the chemical absorption, which depends on the acid-base reaction and, therefore, it requires a solvent of caustic nature. The most common solvents are the amines (mostly the MEA, monoethanolamine) and the ammoniac solutions in the chemical absorption, and the fluorate dissolvent and ionic liquids in the physical. Absorption is capable to separate well the CO₂, since amine notably improves the potential for separation. But, due to the strong interactions produced between solute and solvent (carbonates and bio carbonates are formed) the regeneration process of the amine increases the expenses. Moreover, amines must be diluted in water in order to avoid corrosion problems, what provokes working at very high volumes, which in addition must be heated, adding energetic costs.
- **Adsorption:** Adsorption can appear in packed beds, with materials such as alumina, activated carbons, zeolites and MOFs (Metal Organic Frameworks), and in molecular blocks (monoliths, molecular sieves), with lagged with carbon substratum (Fibre monolith Carbon). In order to represent a competition to absorption technology, the capacity and selectivity towards CO₂ must be very high, and thus the research of adsorbent materials is very meticulous.

- **Membranes:** The use of membranes has become lately a new source of investigation in the field of gas separation. Membranes are selective due to the different relative speeds with which the chemical species penetrate. These differences are due to the permeable molecules size, or due to the solubility and the diffusion (mobility) coefficients in the membrane material. The use of these membranes is complemented with established fundamentals in the absorption or adsorption, depending on the nature of the membrane material.

3.6 CO₂ adsorption materials

As explained so far, one of the most important areas in the CO₂ capture is to find one affine material to adsorb this molecule. This affinity can be divided in the following requirements that would make the material suitable for the separation of CO₂ from a gases mixture: great capacity and selectivity, a fast kinetic during the adsorption and desorption processes, a great physical and chemical stability, and be able to be regenerated at pressures and temperatures which do not mean disproportioned expenses with the global equation.

These would be general conditions for any type of adsorbent material and for any gas. Apart from them, some specific conditions for the concrete capture studied in this assignment can be established, since the conditions in which the carbon dioxide is found in the post combustion industrial gases is known.

These currents have relatively low concentrations of CO₂, which commonly represent 12 to 16% of the total (they are concrete for each process obviously, but it is a very common number in these flows)[4]. Mostly the mixture is formed by N₂ and, furthermore, they are usually found several impurities in a low percentage, such as O₂, H₂O, NO_x and SO_x. Common condition of these currents usually is atmospheric pressure.

In the following section the most promising materials are presented, either the ones that have been in the spotlight for long, and the ones that have been incorporated lately and could be used in the future.

3.6.1 Activated Carbons

This kind of adsorbent is one of the most studied ones, and is already being applied in other types of separations. It consists of amorphous and porous forms of carbons, which have a very

low cost and show a great caloric stability. Its nature has got positive and negative factors for the CO₂ adsorption. In one hand, they have a rather even electric potential, and this means a low enthalpy of adsorption and, therefore, poor adsorption capacities at low temperatures. In the second hand, they have a very high adsorption surface, which allows reaching great capacities of adsorption, as long as it is worked with high pressures. In the CO₂ capture, it obtains good yields in the pre-combustion of gases treatment that can appear at high pressures, but they decrease drastically in the post combustion treatments. Another plus point of the activated carbons is that, due to its hydrophobic condition, they are capable to keep their yields in presence of H₂O, which is usually a very hard impurity to face and that produces many complications in other materials.

Active carbons can be prepared through pyrolysis of resins containers carbons, biomass or fly ashes, and it is continuously tried to improve its benefits increasing its area and porous structure or increasing the alkaline through chemical modifications.



Figure 2. Activated Carbons

3.6.2 Zeolites

They are porous solids which, due to its thermal and chemical stability, they have become one of the leading investigation lines in the research of specific adsorbent materials for CO₂. They are microporous aluminosilicates minerals, which can be organized in very diverse structures. Some of them are from a natural origin and are found in volcanic, sedimentary or metamorphic rocks. These minerals have been used as inspiration of some scientists imaginations, and from them, zeolites have been synthesized in an artificial manner in order to improve the relative benefits of adsorption. In year 2012 they were tabulated 206 types of different zeolites depending on its structure, 40 of them were from a natural origin and the rest of a synthetic origin [5]. They are compounded by tetrahedrons formed by oxygen and silicon

atoms, even though it can also be aluminum or germanium. The ordered structure involves that cavities extend in a regular way.

Zeolites are situated in a privileged place to be utilized in post combustion technologies, since their performance is not linked to high pressures. However, their adsorption capacity decreases a lot in presence of water, since they saturate in a very fast way when vapor is presented in the gas flows.

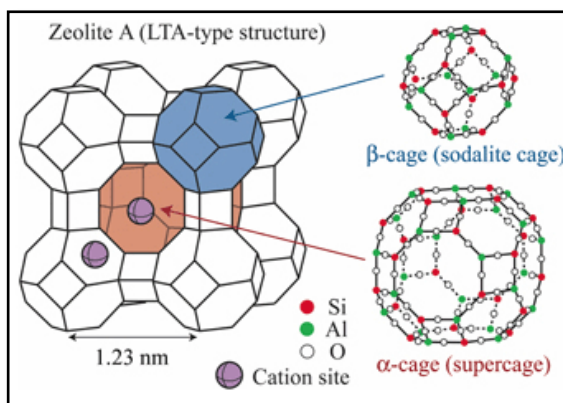


Figure 3. Structure of LTA-type zeolite

3.6.2 Amine impregnated/grafted adsorbents

This group of adsorbents is born with the idea of unifying in a single adsorbent material the positive characteristics of porous solids with the advantages of the chemical adsorption. In one hand, the chemical reaction with amines offers specificity in the CO_2 -solid interaction, and in the other, the porous solids offer a large contact surface that allows reducing the size of the equipment needed to carry out the separation, which avoid the corrosion effect.

The list of support materials for the impregnation or injection of amines is much extended, and it includes silicates, aluminums, zeolites, molecular monoliths, polymeric resins or resins of ionic exchange, among others.

On the other hand, there is also a great variety of amines that can be used, such as the diethylenetriamine (DETA), the triethanolamine (TEA), the pentaethylexamine (PHEA), the disopropanolamine (DIPA), the AMPD and the polyethylexamine (PEI).

So it is observed that there are also many possible combinations of porous solids with amines, and that each of them will have a concrete yield.

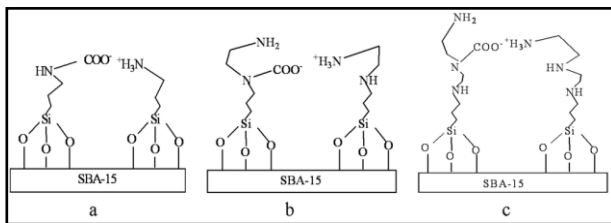


Figure 4. Sta. Bárbara Amorphous type

3.6.4 Metal-Organic Frameworks (MOFs)

MOFs are crystalline materials produced by the linkage of metal atoms or clusters through organic molecules. These materials are synthesized in an artificial way, and they have emerged since the nineties, strengthening itself as one of the most important areas of investigation in the materials science nowadays [6]. It holds the combination of inorganic chemistry with organic chemistry versatility, and the structural benefits of solids.

MOF's structures can be of one, two or three dimensions, and their main property is their great porosity. These pores are kept stable during the molecules elimination, and therefore they can be used to adsorb or desorb gases such as CO₂.

In the MOFs synthesis, one of the most important parts is the selection of the metal and the linkage, as they have very significant effects on the properties that the MOF presents. Then, the metal preference coordination decisively affects the size and the form of pores, since it indicates the number of linkages that can join the metal and it determines the orientation.

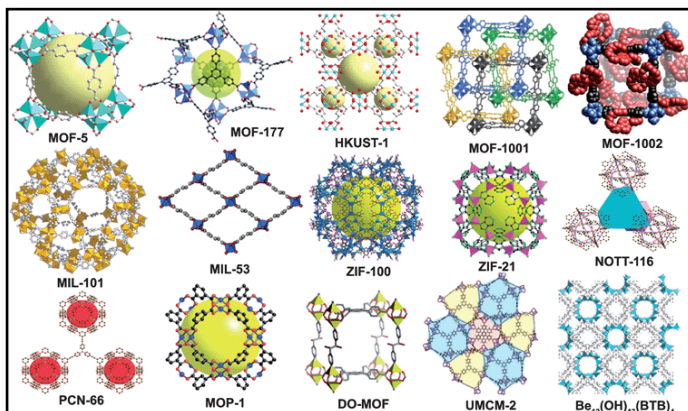


Figure 5. Different types of MOFs

With synthesis techniques such as the isorecticular expansion, there have been successfully prepared materials with the 90% of their space empty, and thus, available for gases storage. These materials densities are very small, around 0.22 g/cm^3 [6]. Moreover MOFs are, nowadays, the leading materials when talking about the specific surface at which crystalline materials are able to achieve. They can reach specific surface values of $6000 \text{ m}^2/\text{g}$, as stated in the bibliography. MOF-210 for instance, shows, following the Brunauer-Emmett-Teller model, a specific surface of $6240 \text{ m}^2/\text{g}$ [6].

Due to all these reasons, the MOFs application in the CO_2 adsorption, in post combustion gases flows is being emphatically studied, although it is important not to forget that, as it is a physical adsorption process, its adsorption capacity is very poor at low pressures, and it increments a lot as the pressures increase. However, their unique characteristics in terms of specific surfaces and porosity are likely to be able to supplement this inconvenience and they situate MOFs as one of the alternatives with more future prospects, although there is still a long way to go before moving them with guarantees to industrial plants.

Several studies have been carried in this sense. MOF-177 for instance, has proved to have very high volumetric capacities of adsorption, with a higher storage density than other materials of different nature such as zeolite 13X. In the other hand MOF-210, synthesized by Yaghi investigation team holds the CO_2 storage record: at ambient temperature and at 50 bars, it adsorbs 2400 mg/g of saturated CO_2 [7].

It must be also taken into account the fact that, one of their most important advantages is the preferential adsorption of water. Then in many MOFs, large adsorptive capacities of CO_2 are overthrown in presence of water during the gases mix.

Furthermore, there are many other relevant facts, such as selectivity. This fact means that the MOFs can become the leaders in the CO_2 adsorption in determined concentrations, conditions and a certain presence of impurities. One of the most interesting MOFs in terms of CO_2 separation in post combustion industrial gases is the Mg-MOF-74. This is the one that is studied in this assignment, and its characteristics are deepened in chapter 5.

Also some MOFs may present particularities in the adsorption process, as some of them deviate from type 1 isotherm (Langmuir), which usually presents zeolites or other more conventional materials. This fact is due to the high structural complexity MOFs are able to reach, and it happens in very concrete cases that present, for example, bio porous structures, it is, with two types of pores of different nature (because of charge, atoms or size). This fact

favors the coexistence of two different adsorption processes, which will modify the standard form of the global adsorption isotherm.

Furthermore, there are many other relevant facts, such as selectivity. This fact means that the MOFs can become the leaders in the CO₂ adsorption in determined concentrations, conditions and a certain presence of impurities. One of the most interesting MOFs in terms of CO₂ separation in post combustion industrial gases is the Mg-MOF-74. This is the one that is studied in this assignment, and its characteristics are deepened in chapter 5.

Last, it must be said that there is a large number of adsorbent materials which are directly linked with MOFs. In the same way zeolites are impregnated with amines in order to improve the adsorption, MOFs can also be functionalized in order to improve certain aspects. Thus, one of the most studied groups for the CO₂ adsorption are the MOFs functionalized with nitrogenous organic groups. They have also been carried out amine functionalizations such as NH₂-MIL-53(Al).

3.7 CO₂ capture technologies at industrial level

All the possible operations to separate CO₂ described above must be placed in a clear manner in the industrial framework, that is, in a certain point during the diverse steps of an industrial process that capture CO₂.

In this sense three technologies can be described, depending on the moment at which the CO₂ cleaning of the residual gases is carried out.

- **Pre-combustion capture**
- **Post-combustion capture**
- **Oxicombustion capture**

Pre-combustion capture is directly linked to the hydrogen production. It consists on the production, from natural gas, of a CO₂ and H₂ principally compounded flow to carry out later on the separation, which is produced in a relatively simple way. Thus, separation is based on the decarbonization of the fuel before the combustion, through gasification techniques. Pre-combustion capture is a much extended technique in the industries around the world with different purposes, and they can also be found cases in which it is specially used in the CO₂ capture, such as twenty ammoniac production plants built recently in China [8], among others.

This kind of capture implies a lower energetic cost than the post-combustion one, as well as smaller dimensions of adsorbers, dissolvent fluxes and stripping consumption of CO₂.

The post combustion capture of CO₂ consists on the separation of CO₂ from the final exit gases, coming from the air cremation of fossil fuels or biomass, without undertaking any operation previous to the combustion. The great interest that this technique generates comes from the fact that the energetic infrastructure around the world is mainly based on processes which imply combustion with air, and they are huge spotlights of polluting gases emissions. We are talking about thermal power plants, refineries, ceramics, cement industries... Thus, post-combustion technology can be easily added to already existent plants in order to reduce the CO₂.

Even though currently, the post-combustion CO₂ capture is not being applied yet in industrial plants, there are many study lines in this sense, and it is called to be a global use technology early. This study is focused on this method.

Last, oxi-combustion, which was born with the idea of increasing the concentration of CO₂ present in the gas flow because then, separation will be easier. One good option to achieve this goal is to remove N₂ to the maximum, as it is usually one of the prevailing elements in the gases mixes every time there is combustion with air. Thus, oxi-combustion consists on the utilization of a variably purity oxygen flow (partially free of N₂) as a flow of fresh oxidizing, instead of air. Then the final flow obtained will be constituted practically by CO₂ and H₂O, and they will be easily separated.

This method however is still in investigation and there are disadvantages that must be worked out, related to the elevated temperatures of flame reached with almost oxygen pure flows.

The diagram in Figure 6 shows these methods:

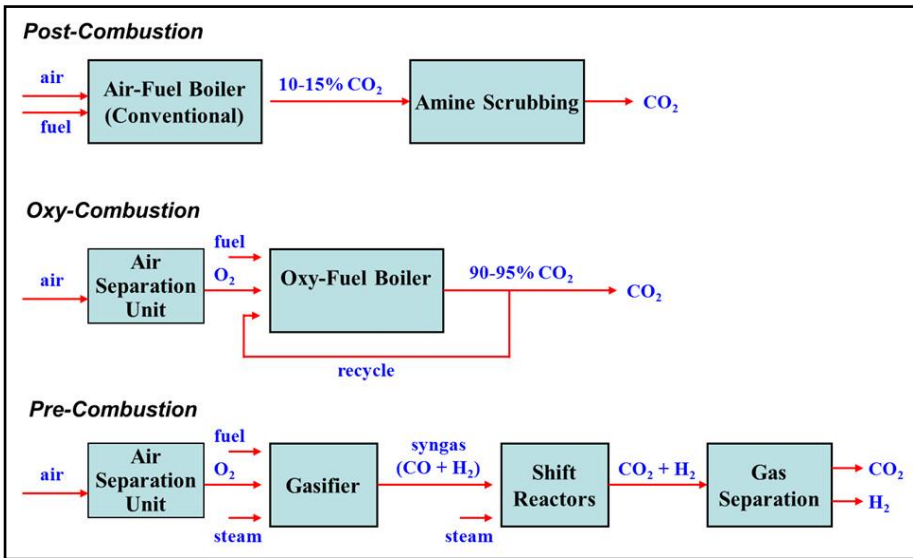


Figure 6. CO₂ capture technologies at industrial level

3.8 Swing Adsorption Process

One of the transcendental parts of the CO₂ separation process is the recovery of the adsorbent material used.

The adsorption process is a discontinuous one. This is, a gas stream enters the adsorption room, with the exit valve open allowing venting of less related gases. When the adsorption bed is full with CO₂, the entrance and exit valve are shut. Then, the P and T conditions in the adsorbent material are changed until it regenerates and pure CO₂ is extracted. This way a cycle is concluded, and the process can begin again. Usually the system consist in several adsorption beds in order to achieve a pseudo-continuum process (see Fig. 7).

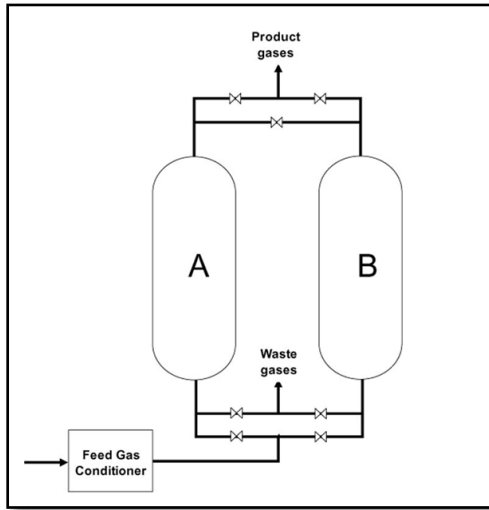


Figure 7. Swing adsorption process

Therefore, the regeneration process is based on the CO_2 desorption, throughout changes in the system conditions. This offers us three main possibilities, which must be studied separately in order to find out which one is more profitable.

These three desorption methods are:

- **Temperature swing adsorption (TSA)**
- **Pressure swing adsorption (PSA)**
- **Vacuum swing adsorption (VSA)**

As can be observed, two of them are related to variations in the system pressures, and the other one is related to temperature changes.

TSA consists on incrementing the system temperature in the moment of desorption. Thereby CO_2 molecules, integrated in the MOF structure, gain energy and no longer have stability inside the pores, and therefore they desorb themselves and the adsorbent material is regenerated. A scheme of the amount adsorbed and desorbed during the process can be seen in Figure 8.

The VSA method consists on reducing the system pressure in order to produce the same effect. As gases have been adsorbed at atmospheric pressure, to desorb them very low

pressures must be reached, very close to the vacuum. The lower it is the pressure, the higher the percentage of CO₂ will be desorbed.

Lastly, PSA is based on the same principal as the VSA, but it proceeds in a different way. Gases are pressurized before entering the adsorption chamber and therefore, they are adsorbed at a higher atmospheric pressure than the previous cases. So, once finished the adsorption process, the only action left is to bring the atmospheric pressure, which can be easily done.

As it can be observed, they all bring an energetic cost attached which is always traduced in economic terms. In the TSA, energy must be applied to heat the system, in the PSA, to pressurize the entry gases, and in the VSA in order to make the vacuum. It must be found out which one of the three methods means a lower energetic cost, taking into account the total percentage of adsorbent that can be recovered in each case.

The working capacity, and therefore the CO₂ quantity able to be separated at each step of the work will depend on the desorption capacity of the chosen system.

However, the best option is not always one of these three, but a combination of them all may offer better results. Thus, in order to reach an optimal process, it could be the case that the best way was to pressurize up to a certain level the entry gases, increase the temperature up to a certain point during the desorption and also in the desorption to reduce the pressure up to a certain level.

Finding this concrete point is an extremely complicated task, since there are many possibilities and a huge number of experiments are needed in order to figure out which is the optimal point between these three methods, which mean the best relation between working capacity and associated cost.

The present assignment compares the three desorption technologies; TSA, VSA and PSA separately and, from the resulting values of all of them some conclusions are extracted.

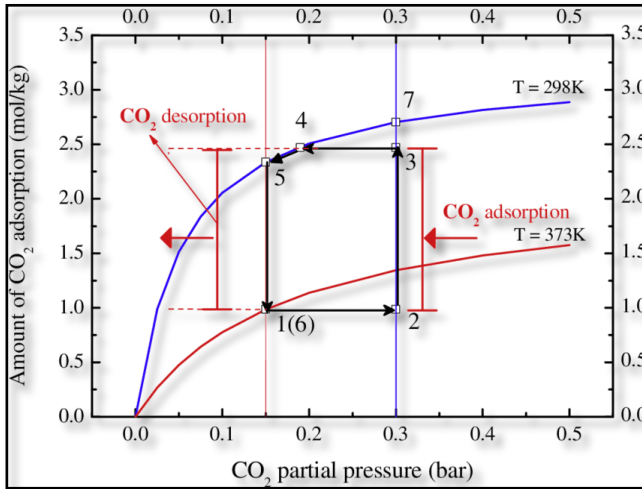


Figure 8. Swing adsorption for TSA

3.9 Outputs for CO₂: Applications and storage

The anthropogenic activity emits annually more than 2500 Gt of CO₂ to the atmosphere [4], from which combustion gases coming from industrial plants are a considerable part. Whether the idea is to separate CO₂ from the rest of gases in order to not throwing it to the atmosphere, it must be decided what will be done with the huge quantities of pure CO₂ that will be gather in every year.

In addition, CO₂ is a molecule with multiple applications in different kinds of industries.

In the food industry it is used as a cryogenic agent in the refrigeration and frostbite processes, as well as it reduces the need of preservatives in packaged products and it is a common ingredient in carbonated refreshments. Besides, in its supercritical state it can be used in the obtainment of caffeine of coffee and tea, the hop of beer, the pesticides existing in cereals or for the cocoa fat extraction.

It is also a good dissolvent for many organic compounds.

In the chemical industry it holds a great utility as a raw material in several productions, and especially in the methanol and formaldehyde synthesis from which it is produced a large quantity, or for the urea, where it is used as an agricultural fertilizer.

It can acquire also a relevant role in the residual water treatment. Moreover, it can intervene in the demineralization of potable waters.

A part from these, CO₂ also beholds applications as a pressurized gas (pneumatic tire, fire extinguishers...) in order to control the pH levels, as a fumigant, etcetera.

Even so, the CO₂ demand is still in a very lower level than its emissions, and therefore, the most part of the CO₂ obtained will have to be stored. There are several storage practices, which vary depending on the subsoil characteristics.

The most common method is the geologic storage. It is the confinement of CO₂ in an adequate geological formation. In order to carry it out, the required technology is very similar to the one used in the oil and gas industry, which are familiar to the injection at profound zones or hydrodynamic thieves, by dissolution, minerals... These proclivity zones for the CO₂ storage can be, for instance, oil or natural gas deposits or deep saline aquifers.

Apart from this one, there are also other less deepened options, such as the biologic storage which refers to the process throughout either marine and terrestrial ecosystems are capable to adsorb the atmospheric CO₂. Last, there is also the possibility of storing CO₂ in oceans. The method consists on injecting CO₂ in the sea bottoms, such that they would be isolated from the atmosphere for centuries. This technology, however, is still in study phase and cannot be undertaken at the moment.

There are already pioneer companies that have started to apply the geologic confinement technique in different places in the planet. The first case was Norway in 1996, and it was built in high seas in order to evade taxes over the CO₂ [8]. This way began the project of storing CO₂ in geologic layer 1000 meters under the sea. Leading companies from Norway, Holland, Algeria, EE.UU, Canada and an increasing number of countries, have followed their steps.

It is estimated that the geologic storage potential of the earth will allow to confine CO₂ during the next 300 years [9].

4. COMPUTATIONAL SIMULATIONS

Molecular computational simulations offer the possibility of studying the behavior of processes such as adsorption and their thermodynamic model, by using codes that solve theoretical models in their total complexity through numeric resolution of the equations involved.

This technique was initially developed during the 1950s, due to the coincidence in time of a remarkable technologic evolution of computers (which has not stopped since then), with studies coming from the atomic bomb development of the second world war and the Manhattan project. Thus the first simulation took place on the MANIAC computer, at the national laboratory of the Álamos, and it was related with probabilistic problems referred to the neutron diffusion in the fission material.

Molecular computational simulation is fundamentally based in statistical mechanics principles. This physics area allows studying the macroscopic properties of a system from their microscopic characteristics, through probabilistic theory.

The microscopic description of a system takes into account the structure of the particles that form it, their interactions and their special ordering.

Taking into account the fact that a macroscopic system studied is composed of 10^{23} order particles (Avogadro's number) we can realize the quantity of parameters that must be valued in order to describe it at microscopic level. On the other hand, very few parameters are needed to specify the macroscopic properties. Therefore it comes off it that knowing the macroscopic parameters of a system is not enough in order to define it microscopically. In other words, there exist a large number of microscopic states compatible with a given macroscopic system.

Statistical mechanics uses two fundamental postulates in order to offer the possibility to studying order 10^{23} systems, examining statistically the properties of much simpler systems.

The first postulate shows that, given a system in equilibrium, each accessible microstate correspondent to the same total energy can appear with the same probability. So it means that

a system in equilibrium does not have preferences for any of the possible microstates that can form it. It is called the postulate of equal probability a priori.

The other postulate is the Ergodic Hypothesis. This hypothesis stipulates that if a system is in equilibrium, the thermodynamic median properties remain constant in time. The methods of computational simulation are supported by the validity of this hypothesis [10], which has already been proven in experimental tests.

Thereby the objective of molecular simulation is the description of a system through a molecular model in order to predict its properties. In addition, apart from reproducing laboratory experiments in computers, it is a complementary tool since it is also possible to prove or deny theories, modifying the parameters in levels that are impossible to be reached experimentally, allow gaining physical insights of the physical phenomenon and also obtaining a graphical view of the process.

Two key methods in the computational simulation have been developed: the Molecular Dynamics (MD) and the MonteCarlo method (MC). The two of them allow generating different configurations of a particles system, but they have some fundamental differences.

Molecular Dynamics is a method of deterministic type, while MonteCarlo is a probabilistic type method. So in molecular dynamics the configurations generation is carried out through the second Newton's law, which enables computing the dynamic properties, whereas the MC follows a stochastic method and therefore it is not possible to carry out a temporal tracing of the system, and it is used in processes that can be described from some random component. Thus the information obtained from Molecular Dynamics is the position and the velocity of each particle of the system in every determined instant, while the MC gives the position of each particle in every step of the simulation.

MD studies microscopic behaviors of the system from the resolution of Newton, Hamiltonian and Lagrange equations. The statistical ensemble that it generates is usually of microcanonic or NVE type (the number of particles, the volume and the total energy are constant), although they can be used NVT or NPT types ensembles, as well. But they do not usually produce many differences in the results, since the different ensembles can induct to small statistical differences, and these are cancelled by thermodynamic limits.

In order to carry out a Molecular Dynamics simulation a group of particles are conveniently chosen by their spatial coordinates, their velocities and their masses. The statistic averages are

computed from the velocities and position, as temporal averages over the system's trajectory. Since the system evolves with time, it will eventually evolve towards the equilibrium

The main difference in the MonteCarlo method is that the position and moment values are generated through random configurations. The most common ensemble of MC method for adsorption simulations is the grand canonical μVT (fixed chemical potential, volume and temperature).

The bases and methodology followed to generate the configurations in the MonteCarlo method will be studied in deep in the following section, since it is the method that has been used in the molecular simulation of this work.

However before this, a set of molecular simulation characteristics common either in the MD and the MC will be reviewed, as it is convenient to know them and to take into account in order to obtain reliable results.

Molecular simulations can be divided in three steps.

In first place the initialization step, which corresponds to the selection of the potential type, the ensemble of the system and it also includes the specification of the contour conditions and the initial conditions such as temperature, volume or position of the particles in the instant 0 of the simulation.

Secondly there is the configurations generation step. This is the point where the two simulation methods differ, and therefore in this case we will focus on the MonteCarlo method.

The last step is the results analysis. In this headland it is pretended to evaluate the system properties through the acquired information. Thereby, the microscopic results obtained are transferred to physical macroscopic properties, which are divided into static, dynamic and thermodynamic properties. This action is carried out through temporal averages or through simulation steps of the different configurations. Thus, considering a lapse of time or a number of steps large enough, these average values correspond to macroscopic values, considering an ergodic behavior of the system.

Static properties are described throughout the pars distribution and through the static structure factor. With regard to the thermodynamic properties, T is computed as the average of kinetic energy by means of the equipartition theorem and the average P is computed by means of the virial theorem. Other properties such as specific heat or elastic constants are computed from median quadratic fluctuations. Thermodynamic properties like entropy and free energy are

obtained from much elaborated methods [10]. Dynamic properties are exclusive of molecular MD, since the MC does not respond to a temporal dynamic of the system.

4.1 Interatomic potential

Interatomic potential is very important in the simulation, since from its fidelity to reality depends directly the quality of the obtained results. The more detailed it is, the better the simulation will be, but the functional complexity of the potential and the required time of simulation will increase. Therefore, a compromise must be reached in which the used potential enables obtaining enough reliable results, in an appropriate period of time.

In first place it must be said that both methods are carried out using classical mechanics equations. This fact itself already represents an approximation, since the exact method to study the microscopic systems is the quantum mechanics, by solving the Schrödinger equation for a system of interacting particles. This approximation is very good in most of the cases, but in some punctual cases a more accurate system must be found.

A polyatomic molecule can have three kinds of movements: translational, rotational and vibrational. Classical mechanics describe precisely the movement of translation and rotation. The rest of movements of vibration-oscillation, which can appear in adsorbents, are associated to the ions in the structure. Whether these vibrations are harmonic, the obtained frequencies by classical mechanics coincide with the quantum methods. But if they are not harmonic, the classical methods require corrections. Some studies have been carried out to modify MD and MC to adapt them to these concrete cases, such as in the Car-Parrinello method of the MD, and the QMC (Quantum MonteCarlo) [11]. However, as we have said, these methods hold a very high added value of calculus period and it is inconvenient to use them when it is not strictly necessary, and for systems at ambient close temperature the classic methods are considered to be the proper ones.

In traditional mechanics, in a system of N atoms, potential energy can be expressed from the atoms individual coordinates, the distance between two of them, the relative position between three atoms and so on.

$$\mathcal{V} = \sum_{i=1}^N v_1(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j>i}^N v_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j>i}^N v_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots$$

The first one represents the interactions of a body (external force), the second one the interactions of two bodies, etcetera.

The term that represents the interactions between two bodies only depends on the module of inter atomic distance $|r_1 + r_2|$, and it is very important since it has been proven that it itself can describe really well certain physical systems, as it is the case of Lennard-Jones potential for noble gases. The rest of effects are the result of many bodies' interactions.

On the other hand, the values of the forces of each one of these terms must be determined. In this sense different force fields can be found, defined in the bibliography, which may differ slightly due to different considerations in functional forms used to describe the interactions and parameters used to describe the functional forms.

The total energy of the system can be divided between the contributions of two different parts. On one hand it can be divided in the interactions of linked atoms and, on the other one, in the interactions between non-linked atoms.

At the same time, in a force field, from the classical point of view, these energies can be subdivided. The interactions between non-linked atoms are bond stretching forces, bond bend and dihedral torsion, and the forces between non linked atoms are contributions of the van der Waals forces and electrostatic interactions. Therefore potential energy of the system can be expressed in the following manner:

$$U_{total} = U_{bonded} + U_{non-bonded}$$

$$U_{bonded} = U_{bond} + U_{bend} + U_{torsion}$$

$$U_{non-bonded} = U_{LJ} + U_{electrostatic}$$

Sometimes however, more sophisticated systems that incorporate other kind of forces are used.

The value of these parameters can be obtained either through the adjustment with respect to experimental data from densities, adsorption heat, vaporization heat, or by the adjustment of parameters derived from quantum studies.

On the other hand, interactions between non-linked atoms are especially important in the adsorption processes study, since they are the ones that appear between the atoms of the adsorbed substance and the atoms of the adsorbent material. They are of physical type, it is, the ones that appear between atoms which relate within them without being chemically linked.

These forces are divided in two main groups:

Van der Waals forces: These forces act in both senses, the attractives are due to the instant fluctuations of moments of electric dipoles between adsorbed and the adsorbent surface, while the repulsive ones come from the superposition of the electronic cloud between molecules and the adjacent surfaces. These forces are combined and give a total potential energy which are solved through different models such as the repulsive spherical potential, the Morse potential, the EAM type potential, and the Lennard-Jones potential, being this last one the most used in MD and MC, and that can be written in the following way.

$$U(r_{ij}) = B_{ij} \sum r_{ij}^{-12} - C_{ij} \sum r_{ij}^{-6}$$

Where B and C are constants characteristic of the gas-solid system, r represents the distance between i atom and j atom, and where the part elevated to -6 of the Lennard-Jones (LJ) potential pertains to fetching forces, while the part elevated to -12 corresponds to repulsion forces.

The LJ model describes the interaction within two atoms, either at short or long distances. In it, each atom is considered as an indeformable solid sphere. In this type of potential the only existent interactions are the collisions between the system particles, what makes it really useful to describe the fluids behavior in complex geometries or the interaction of different fluids.

Several models are extracted from this expression to express interactions of LJ from already known data. The most common is the following:

$$U_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ji}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ji}} \right)^6 \right]$$

Where ε is the depth of the potential well and σ is the finite distance at which the inter-particle potential is zero. These parameters can be seen in Figure 9, which shows the potential energy variation of an atom physically adsorbed, in correlation of the distance r , to which the adsorbent is situated: . Both σ and ε are specific of each concrete type of atom. Their values must be known in order to carry out the simulations.

As it is appreciated, the potential consists of two terms that predominate at short or long distances, depending on the immediate interaction of the particle in the system. The first term with higher exponential prevails for attractive long-distance interactions. The combination of the two members of the equation describes the interaction at the equilibrium distance of the equation.

Moreover, for interactions between different atoms, such as the ones between the adsorbent and the adsorbed, the Lorentz-Berhelot combining rules are generally used:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

As it can be observed, at very small distances the potential energy of the particle is high, since repulsion forces predominate. There is a concrete point where the atom is close enough to the adsorbent surface to have very attractive forces, and where the repulsive forces barely have value (which increase exponentially from a certain distance, close to this point). It is in this point, the minimum one, in which the atom becomes stabilized and, therefore, adsorbed.

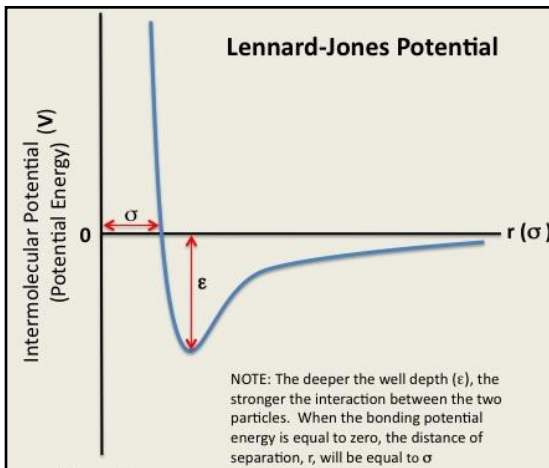


Figure 9. LJ potential

Furthermore, the fact that the potential vanished at very long distance values enables to truncate the calculus from a certain radius. So the computer will do the calculus of LJ potential only when the distance is smaller than the established (radius cutoff), and when this is higher the computer will directly assign it the value of 0. This way the computational efficiency is considerably improved.

Electrostatic forces: These forces are described through the potential equation of Coulomb:

$$U_{elect}(r_{ij}) = \frac{1}{4\pi\epsilon_r\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

Where ϵ_r is the electric constant of the habitat where electric charges are allocated, ϵ_0 is the permittivity in the vacuum ($8,85 \cdot 10^{-12} \text{ C}^2 \text{ S}^2 \text{ kg}^{-1} \text{ m}^{-3}$), q_i i q_j are the charges of the involves atoms, and r_{ij} is the distance between them.

It must be taken into account that the partial charge over a certain atom is usually considered constant, as the polarization effects are negligible. Compared to LJ (r-6) potential, the electrostatic interaction potential is much higher (r-1). Furthermore in this case it cannot be used the simple truncation because these interactions are produced at large distances. Electrostatic forces, in addition, are much more costly to calculate than van der Waals forces, since the integral of the volume potential diverges. Therefore, to compute them it is used the Ewald sum method which [10, 12], even though it is very accurate and precise, it consumes a lot of calculus potential.

4.2 Contour conditions and potential truncation

The simulation occurs in the so called simulation cell, and its volume must be chosen properly. If what occurs at microscopic level in a determined system is reproduced, it is necessary to choose the contour conditions which simulate an infinite environment of particles around the particles of our system, minimizing to the maximum the effects of the limit of our simulation cage. In order to achieve this effect, the so called periodic contour conditions are used, where from a primitive cell, an infinite and periodic network of identical cells is configured [13]. In the figure below it can be appreciated an example of a periodic simulation of two dimensions. It can be differentiated the imaginary limits of each cell and, in the blue box, the

particles that interact the most with the central image, which are the ones that take into account the criteria of the minimum image.

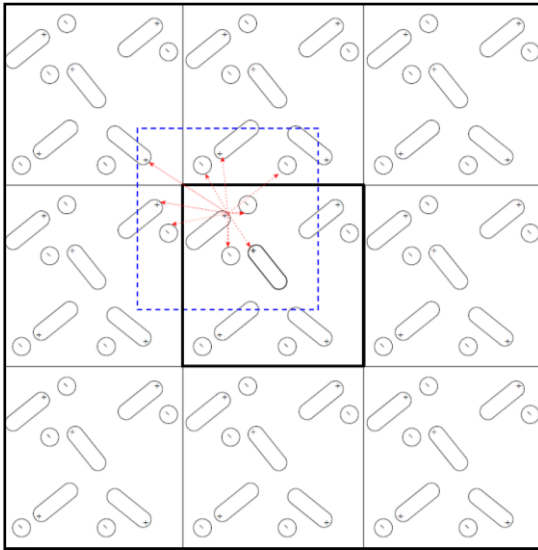


Figure 10. Periodic Bulk conditions

In this way a particle does not interact only with the rest of particles of the bulk, but it can do it with all the particles of each periodic replica.

But if we consider that all the particles interact within them, the potential of each one will depend also on the forces produced between all the particles. Compute this potential seems an almost impossible task, since the number of factors to take into account is exaggeratedly huge. But as it is known that interactions are proportional to the distance between particles, in the final value of the potential will only contribute decisively the closer particles, while the farther are negligible in practice.

From this idea emerges the truncation of potential concept. The truncation potential is nothing else than establishing a cutoff radius from which the interactions of particles outside this radius are not calculated, and they are directly given a value of 0. This fact enables to reduce a lot the simulation time.

One of the many possible criteria to select the cutoff radius has been advanced in the description of the previous figure and it is the convention of the minimum image. This method

requires the potential to be lower than the half length of the cage, since it consists on that, around every particle of the system, it is constructed an imaginary box of the same dimensions of the replicated bulk, and it is considered that only the particles inside this box will interact with it.

However, in this system there is also a computational cost, which can be avoided. In order to carry out the cutoff, the distances between all the pairs of particles in the system must be calculated.

Some methods have been figured out in order to avoid this calculation, on the basis that between a simulation step and another one, the number of neighbor particles with which an atom interacts does not significantly varies. The most common one is the Verlet method [10].

4.3 MonteCarlo's method

MonteCarlo's method is of probabilistic nature, since it carries out an intensive use of random numeric generators in its performance. In fact, this method's name comes from MonteCarlo casinos, which represent the games of chance capital. The invention of this method is attributed to John Von Neumann and Stanislaw Ulam, being the last one who has explained that he came up with the idea while he was playing Solitaire in 1946. He realized that it is much easier to have an idea of the general result of Solitaire doing several tests with the cards and counting the proportions rather than computing all the possible combinations. He decided to transfer this idea to his neutron diffusion work in the Los Álamos laboratory, harnessing the computers capacity in order to generate thousands of possibilities and, because of them, being able to describe a physical process through random combinations probabilistically distributed.

In the following lines, the configurations generation method is deepened.

According to statistical mechanics, the thermodynamic value of a property is:

$$\langle \mathcal{A} \rangle_{total} = \frac{\int d\mathbf{p}^N d\mathbf{r}^N \exp[-\beta\mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)] \mathcal{A}(\mathbf{p}^N, \mathbf{r}^N)}{\int d\mathbf{p}^N d\mathbf{r}^N \exp[-\beta\mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]}$$

Then, and considering that usually the part of kinetics energy of K from Hamiltonian depends in a quadratic way on the p moments, these degrees of freedom can be integrated quadratically. So the expression remaining only depends on the r coordinates.

$$\langle \mathcal{A} \rangle = \int d\mathbf{r}^N \mathcal{A}(\mathbf{r}^N) \mathcal{Z}(\mathbf{r}^N)$$

$$\mathcal{Z}(\mathbf{r}^N) = \frac{\exp[-\beta \mathcal{U}(\mathbf{r})]}{\int d\mathbf{r}^N \exp -\beta \mathcal{U}(\mathbf{r})}$$

To this point, the problem that appears is that, given the potential energy, the probability function must be computed and afterwards the integral must be solved. This is a multidimensional integral ($6N$ dimensions where N is the number of particles), and therefore solving by means of quadratic methods is too costly. As alternative, the MonteCarlo method is used in order to solve it.

Accepting the fact that we are capable of randomly generating points in the configuration space in accordance with the probabilities distribution, it is known that in average, the number of points generated per unit of volume around a certain point, is the product of the total number of points generated by the probabilities distribution.

$$\langle \mathcal{A} \rangle = \frac{1}{L} \sum_{i=1}^L n_i \mathcal{A}(r_i^N)$$

But, since the distribution of probabilities is proportional to the Boltzmann $\exp(-\beta U)$ factor, the points with low energy contribute significantly, while high energy points will have a very low relative weight. So then the key lies in thinking off a method which generates points with a high relative weight. This enigma was resolved by Metropolis in the fifties decade.

His solution is based on the generation of random configurations in accordance with the stochastic process of Markovskiy. The generation of the configurations through the construction of a Markov sequence means that the probability for an event to happen depends on the immediately previous event [10,12].

Transferred to MonteCarlo's method, this translates into a process with a set of random steps. It is constructed in a way that the probability of finding a particular state of the system is proportional to the Boltzmann factor.

The method works in the following way: From a certain configuration, a sample movement it is carried out which changes the system state. Depending on in the new of the system and on a random number, the new state is accepted or rejected. The acceptance rule of the system is constructed in a way that the probability for the system to adopt a certain configuration is proportional to its statistic weight.

Then the next step of the simulation consists on the translation and rotation movements of particles randomly selected.

For the translation movements the molecule moves in accordance to a vector of the type:

$$x_i(n) = x_i(o) + \Delta(Random - 0.5)$$

$$y_i(n) = y_i(o) + \Delta(Random - 0.5)$$

$$z_i(n) = z_i(o) + \Delta(Random - 0.5)$$

The term Δ means the maximum possible shift, and it must be chosen in order to obtain a reasonable fraction of accepted movements. If it is very small, many movements will be accepted, but the sample of the phase space obtained will be biased. Instead, if it is too big, most of the shifts will be rejected. Therefore, the optimal value of Δ depends on the characteristics of the interaction potential.

The rotational shift works in an analog way, generating a random rotation of the type:

$$r' = \begin{pmatrix} \cos\Delta\theta & -\sin\Delta\theta & 0 \\ \sin\Delta\theta & \cos\Delta\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot r$$

In this case, the maximum rotation angle is chosen in order to, approximately, 50% of the sample movements, be accepted.

In addition to this it must be considered that in the great canonical MonteCarlo, the number of molecules present in the system is not constant. Thus, an acceptance or rejection rule of the entrance or exit of molecules of the system must be determined. This rule, in this case is base

on the new potential obtained after the movement, if it is negative the shift is accepted, but if it is positive the shift can be accepted or rejected depending on whether its product by a random number is higher or lower than the $\exp(v(r_{ij})/kT)$ expression.

Thus, the outline of the configurations generation procedure according to metropolis algorithm is structured as shown below in the translational movement [13].

1. Any particle n is selected and its energy is computed. $U_i(r)$.
2. The particle is given a random movement $r' = r + \Delta r$ and the new energy is computed $U_i(r')$.
3. - If $\Delta U < 0$, the change is accepted and it goes back to step 1.
 - If $\Delta U > 0$, a random number is chosen between 0 and 1.
 - If $< \exp(\beta \Delta U)$, the change is accepted and it goes back to step 1.
 - If $> \exp(\beta \Delta U)$, the change is not accepted, it is, the initial position of the particle is maintained, and it goes back to step 1.
4. Once this process has been carried out with all the particles, the configuration obtained is kept and it goes back to step 1 to start a new cycle. After a determined number of steps, an equilibrium is reached and we can advances towards step 5.
5. The physical properties of interest are calculated from the configurations kept.

A similar process is carried out with rotational movement and with the entrance and the exit of the particles of the system.

5. METHODOLOGY AND SIMULATION DETAILS

In order to be able to carry out a reliable simulation, a forcefield that enables obtaining potential energy from the system at each step of the simulation must be defined. This forcefield must describe reality with the maximum possible precision. To do so, it is needed to know in deep the Mg-MOF-74 structure, since this forcefield depends directly from the nature of the atoms that form it and from its disposition.

The Mg-MOF-74 structure is formed by carbon, hydrogen and oxygen atoms, linked to magnesium metal centers. This and the rest of MOFs with M-MOF-74 form (where M can be Mg, Zn, Co or Ni atoms), are obtained from the solvothermal synthesis at temperatures between 100 and 125 °C [14]

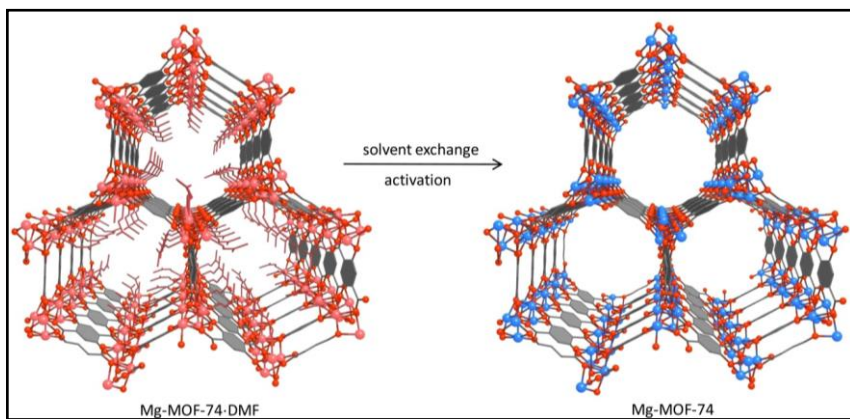


Figure 11. Mg-MOF-74 structure. Blue, red and gray colors for magnesium, oxygen and carbon atoms, respectively.

For the description of the force field, the Lennard-Jones 6-12 model has been used, combined with the Lorentz-Berthelot rules (see chapter 4.1). But for the assignment of LJ epsilon ϵ_{ij} , and sigma σ_{ij} values and also the charges, it is not enough to know which is the atom, but it also depends on the rest of atoms to which it is bonded. This is due to the fact that at quantum level, the attractive and repulsive forces are affected by nearby atoms, and

therefore, it is not the same in terms of potential energy calculation, one carbon atom linked to a carbon or hydrogens atoms, that one carbon atom with a linkage with magnesium. Therefore for the Mg-MOF-74, three different oxygen atom types are defined according to their allocation in the space, four carbon atoms, one hydrogen and one magnesium atom. This idea is illustrated in the picture below:

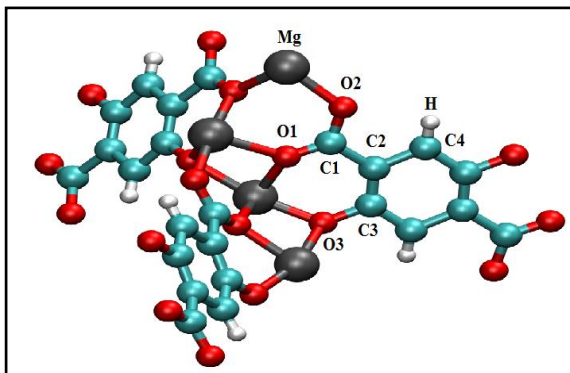


Figure 12. Different atoms types in Mg-MOF-74

LJ and charges parameters assigned to each atom are shown in the table below, extracted from the bibliography [15].

Table 1. LJ parameters and charges for Mg-MOF-74

Atoms	Lennard-Jones		
	ϵ_{LJ} / k_B (K)	σ_{ij} (Å)	Charge
O1	30.190	3.118	-0.871
O2			-0.768
O3			-0.805
C1	52.840	3.431	0.930
C2			-0.481
C3			0.467
C4			-0.382
H	22.140	2.571	0.233
Mg	55.850	2.691	1.678

What is left now is to define these parameters for the species that will be adsorbed, and which will be of a different nature and that will interact with MOF's atoms. The molecules studied in this work are the CO₂, the N₂, NO₂, NO, SO₂ and O₂.

In specific for O₂ and N₂, since they are molecules with a double link, at practical level they behave as if they had a mass center between them. Then, in order to be able to properly define their behavior, we are considered as N--X--N and O--X--O type molecules, where X is considered as an imaginary atom of the molecule (dummy atom), with an own charge.

The used parameters for these molecules are the following [16,17,18,19]:

Table 2. LJ parameters and charges for adsorbates

Adsorbate	Atoms	ϵ_{LJ} / k_B (K)	σ_{ij} (Å)	Charges
CO ₂	C	27.000	2.800	0.700
	O	79.000	3.050	-0.350
N ₂ (N-X-N)	N	36.400	3.320	-0.405
	X	-	-	0.810
NO ₂	N	50.360	3.240	0.146
	O	62.510	2.930	-0.073
NO	N	79.500	3.014	0.029
	O	96.940	2.875	-0.029
O ₂ (O-X-O)	O	54.350	3.050	-0.112
	X	-	-	0.224
SO ₂	S	145.900	3.620	0.471
	O	57.400	3.010	-0.235

For the bond distances, we have that, $r = 1.16$ Å for CO₂ (C--O), $r = 1.10$ Å for the N₂ (N--N), $r = 1.20$ Å for the NO₂ (N--O), $r = 1.15$ Å for the NO (N--O), $r = 1.21$ Å for the O₂ (O--O), and $r = 1.43$ Å for the SO₂ (S--O). The bond angle of NO₂ (O--N--O) is 134.3°, and of the SO₂ (O--S--O) is 119.5°

All these are necessary parameters to define each new configuration of the system, it is, each simulation step. Each step holds changes that are given by the translational and rotational movements of the molecules, as well as by the insertion/deletion of gas molecules in the system.

In this assignment, for each simulation 1,000,000 steps of MonteCarlo have been carried out for each simulation. From the plots of adsorbed molecules vs the number of steps, which are shown in appendix 2, it has been considered that 500,000 first steps are necessary to reach an equilibrium point of the system in a clear way. From the rest of steps, from the step 500,000

to 1,000,000, it has been undertaken an arithmetic median of each data of interest in order to obtain a reliable value.

In order to accomplish the task of this assignment 92 different simulations have been carried out in the open source LAMMPS software. They are distributed in 68 simulations for pure gas flows, and 24 for the binary and ternary mixes studied.

Simulation provides values such as the number of atoms adsorbed of each species of interest, from which the moles adsorbed per kg of MOF are extracted through a conversion factor using specific values of the Mg-MOF-74, such as density.

The table 3 shows the Mg-MOF-74 necessary values in order to accomplish this calculations, and other parameters required for the energy consumption in the TSA, PSA and VSA processes, obtained from the bibliography [20].

Table 3. Properties of Mg-MOF-74 and other parameters

ρ (density of the Mg-MOF-74)	914.88 kg/m ³
C_p (Mg-MOF-74)	0.896 kJ/kg·K
V of the bed	1 m ³
ϵ (voidage of bed)	0.4
η (efficiency)	0.75
k (polytropic parameter of gases)	1.35
R (gas constant)	8.314 kPa m ³ / kmol K

As mentioned in section 3.3.1., the isosteric heat is a thermodynamic property characterized by the enthalpy variation associated to desorption of a molecule at the surface. From molecular simulations the following equation can be used [21], according to the energy/particle fluctuations in the grand canonical ensemble.

$$-q_{st,A} = \frac{\langle U \times N \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} - \langle U_g \rangle - RT$$

Where U is the total potential energy of the system per molecule, N is the number of molecules adsorbed, U_g is the energy of an isolated guest molecule, and the brackets $\langle \dots \rangle$ denote an average in the GCMC ensemble.

In the section of swing adsorption process results, the calculus of work w (J) in the PSA and VSA processes is obtained form:

$$w = \left(\frac{k}{k-1} \right) \frac{R T}{\eta} N \left(\left(\frac{P_{out}}{P_{in}} \right)^{\frac{k-1}{k}} - 1 \right)$$

Where k , R and η are described in the previous table and T is the temperature of 313K of work.

P_{in} represents the pressure at which the adsorption process is carried out and P_{out} , the pressure at which the regeneration is executed. For the PSA process evaluation, P_{in} has a value of 10 atm and the P_{out} a value of 1 atm in this work. However for VSA process we have evaluated two desorbing conditions: the P_{in} has a value of 1 atm, while P_{out} has been evaluated for 0.1 and 0.05 atm.

The N symbol is defined, in the PSA, as the quotient of working capacity of CO₂ divided by the partial pressure of this gas: $N = \frac{\Delta q}{Y}$

However for the VSA and TSA processes it is defined as the sum of the quantity adsorbed of the different components of a mix: $N = \Delta q_1 + \Delta q_2 + \Delta q_3 + \dots$

N is defined in that way since we assume that the adsorption/desorption process does not include a purge step to completely regenerate the bed.

For the calculation of TSA energy requirements, we use the following expression:

$$Q = m \left(C_p \Delta T + \sum q_{st} \Delta q \right)$$

Where m is the mass of the MOF, C_p is the heat capacity and ΔT the increment of temperature, which goes from 313K in which the adsorption is performed, to 383 and 443K, which are the two temperatures at which regeneration has been studied.

6. RESULTS AND DISCUSSION

6.1 Validation

First of all, a validation task of the used method has been realized in order to make sure that the implemented simulation models are correct. To do so, different calculations of a pure flow of CO₂ have been carried out, in order to obtain the isotherms from temperatures of 313, 383 and 443K, as well as one calculation of pure N₂ at the same conditions. These results have been compared with laboratory experimental results of the adsorption of these gases in the Mg-MOF-74 [22]. In the figures 13 and 14 we can observe the results obtained.

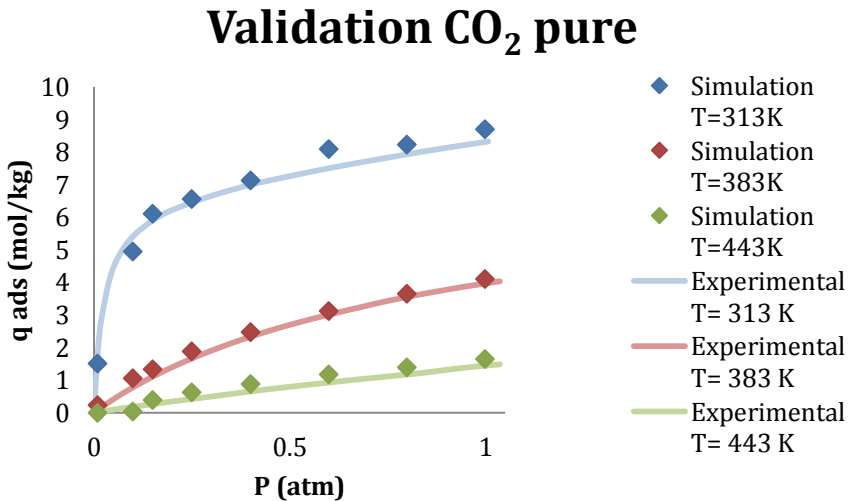


Figure 13. Validation CO₂ pure

Continuous lines represent the isotherms obtained experimentally, while the further points are the values obtained in the simulation. As it can be noticed they are correspondents. Therefore, the method employed in the simulation is precise, and the results achieved in this work are rigorous and faithful to reality.

In the validation of pure N₂, identical results have been reached [22].

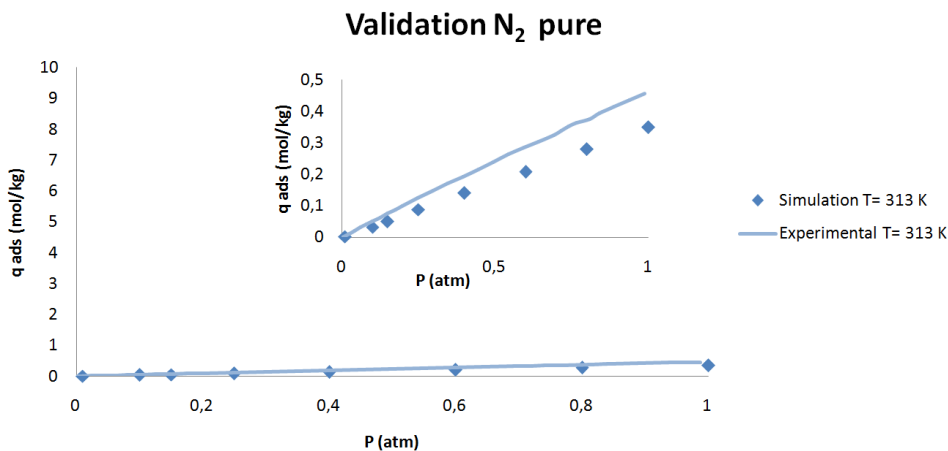


Figure 14. Validation N₂ pure

6.2 Pure isotherms

Adsorption simulations for different pure components have been undertaken and are depicted in Figure 15. These elements have been chosen by their habitual presence in the post-combustion gases flows, and thereby, due their potentiality to act as impurities in many CO₂ separation processes. These components are the O₂, NO₂, NO and SO₂. In the lines that follow, the isotherms of these pure components obtained at 313K are introduced. These isotherms have not been compared since experimental data has not been found.

Pure isotherms cannot show us how a certain gases mix will behave, but by means of them, we can think of which are the species that will imply more problems when working with impurities.

Due to this fact, conclusions shall be prudently extracted, since there are many factors in a gases mix able to destabilize the achieved results in several pure isotherms, due to the interactions within new particles which compete to be adsorbed, and which may provoke inhibition problems or, instead of that, in some gases, to promote and foster their adsorption or the adsorption of another present molecule.

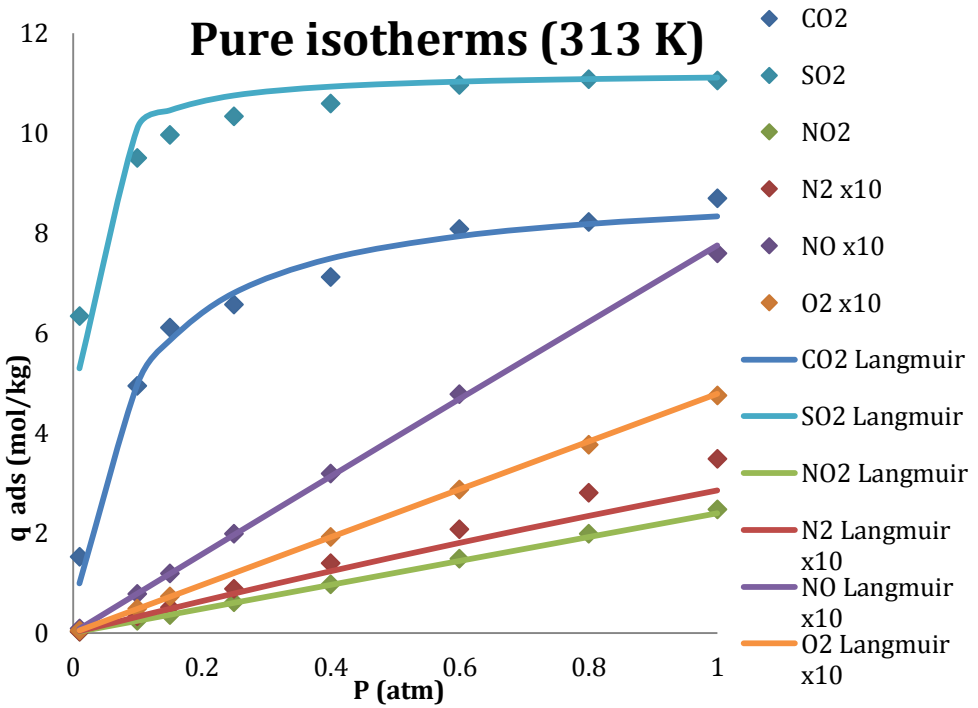


Figure 15. Pure Isotherms

The most relevant fact observed is that in the Mg-MOF-74, the CO₂ is much adsorbed than the rest of impurities, with the exception of the SO₂. This shows that Mg-MOF-74 is really affine to carbon dioxide molecules, and it situates adsorption at ranks between 6 and 9 mol/kg at pressures between 0.1 and 1 atmospheres and at 313 K. The only studied molecule that shows more affinity to be adsorbed in the MOF's pores is the SO₂, situated above with an adsorption around 11 mol/kg. Thus it can be guessed that SO₂ will be the most problematic impurity. From the other impurities, since they are adsorbed at much lower values at the same conditions, it is presumed that they will not affect too much in the total adsorption of CO₂. In fact, it must be clarified that N₂, NO and O₂ molecules in the graphic have been mega scoped in a factor of 10 in order to enable to properly appreciate their trend. So, apart from SO₂, NO₂ is the most adsorbed species, although at a large distance, which makes sense since it is the molecule that bears the most similar characteristics with CO₂ and SO₂. It is important to outline as well that

one of the less affine species is the N₂. It is a relevant fact, since nitrogen percentages are really high in the industrial gases flows, and an adverse result with respect to nitrogen would be a reason strong enough to reject an adsorbent material

On the other hand, we can notice another relevant issue surveying the form of isotherms. CO₂ and SO₂ have the same isotherm type, which perfectly adapts to the type I isotherm (see chapter 3.1.2). However, the rest of elements which seem to be following a linear behavior, show an isotherm that turns around towards type III isotherm (The curve cannot be noticed due to the rank of pressures of the experiments, but if the pressure was significantly increased, the similarity would be observable). This fact agrees with the conclusions achieved until now, as the type III isotherm appears in processes where adsorbent and adsorbed are very little affine within them.

Adjustments of the isotherms have been carried out through the Langmuir method, and the obtained equation for each element has been plotted in the graph as a continuous line. As it can be noticed, it coincides perfectly with the simulation values obtained, represented by points. The correlation reached with Langmuir method is very high. The results of constants, as well as the equation of each line and their correlation obtained for CO₂ and SO₂ are presented in the Appendix 1.

With the data of the pure isotherms, it can be also obtained the isosteric heat q_{st} , which represents the quantity of energy is needed to apply to the system in order to extract the adsorbed molecule (see chapter 3.3.1). To understand how the isosteric heat varies with the quantity of material adsorbed, the following graph (see figure 16) has been plotted.

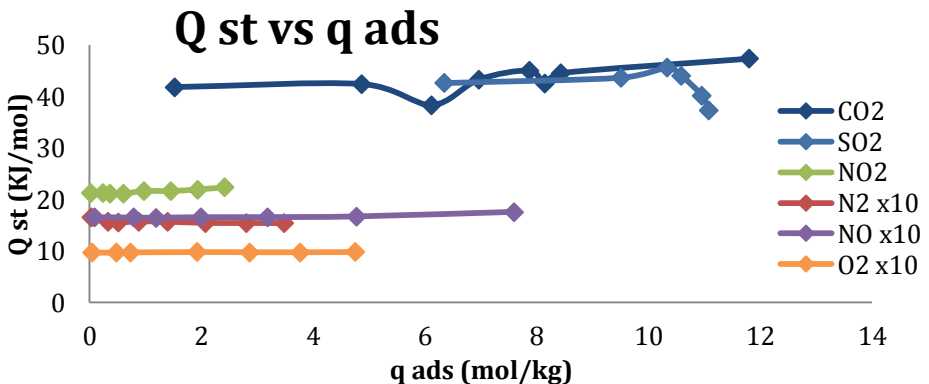


Figure 16. Q_{st} vs q_{ads}

For a proper interpretation of this graph it must be reminded that q_{ads} of NO, N₂ and O₂ molecules have been ten times over dimensioned in the x axis.

It can be realized that isosteric heat is a property which remains practically constant with q_{ads} . Keeping the previous trend, CO₂ and SO₂ are, by far, the ones with more isosteric heat, which means that they will be the more difficult to desorb during the regeneration. Obviously, if they are the most affine to the MOF, they will be the more difficult to extract. It must be remarked, however, that the variations and deviations observed in the CO₂ and the SO₂ may be due to the changes in the nature in which they have been adsorbed and, even though it is out of the scope of this work, we believe that their study could enlighten the adsorption process that occurs in these molecules.

6.3 Binary and ternary gases mixtures

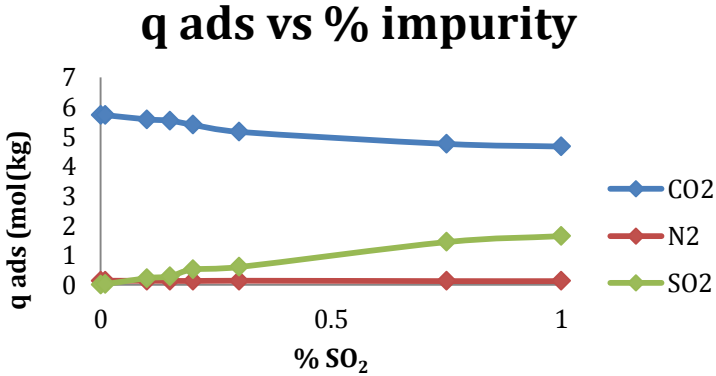
Once studied the performance of Mg-MOF-74 in these components separately, it is necessary to see how it behaves in front of percentage mixes of all of them.

In the present dissertation it has been studied the CO₂ adsorption by Mg-MOF-74 in a gas flow compounded by 85% of N₂ and 15% of CO₂, which is a very common proportion. Furthermore, it has been considered the presence of an impurity with a percentage weight inside the mix between 0.001% and 1% [4]. The increase of the impurity percentage is in detriment of the same N₂ percentage. This study has been carried out for the NO impurity on one hand, and for the SO₂ on the other.

6.3.1 Ternary mixtures including SO₂ as impurity

In order to understand how the increase of SO₂ quantity is affected in the total adsorption of CO₂, figure 17 shows the quantity adsorbed in the MOF of the three current elements in front of an increase of the SO₂ presence. Being the first point free of impurities, it is, the binary mixture between CO₂ and N₂, and increasing progressively the quantity until it represents 1% of the total.

The simulations in which the graph is based have been specified at a total pressure of 1 atm, and at a temperature of 313K.

Figure 17. q ads vs % SO₂ impurity

As it was expected SO₂ performs a negative influence in the total of CO₂. Even so, at so low percentages it does exert a decisive influence in the process, since the quantity of the CO₂ adsorbed is reduced considerably. The q ads CO₂ for the Mg-MOF-74 in the binary mixture with nitrogen without impurities is 5.73 mol/kg, whilst with 1% of SO₂ it is reduced up to 4.67 mol/kg. We must take into account that at 313K temperature and 0.15 atm pressure (which is the partial pressure that has the CO₂ in this mix), the q adsorbed for the MOF of a pure flow of CO₂ is 6.11 mol/kg.

It can also be observed that the N₂, even though it is by far the higher molar fraction in the total, it is barely adsorbed, since it holds a very low affinity towards MOF in comparison with the affinity of the two other species. So it remains almost constant and goes from 0.14 to 0.12 mol/kg adsorbed. The q adsorbed of N₂ at 313K and 0.8 atm (the closest simulation to the partial pressure that represents) is 0.28 mol/kg. These data, and also the ones of the quantity adsorbed of SO₂ in a pure flow (pressure 0.01 atm and 313K), and in the ternary mix with 1% of impurity, are shown in the table below.

Table 4. Comparative adsorptions (SO₂ impurity)

	q ads (mol/kg)		
	Pure	Binary Mix.	Ternary Mix. (1% SO ₂)
CO ₂	6.11	5.73	4.67
N ₂	0.28	0.14	0.13
SO ₂	6.34	-	1.65

With these data, another parameter of interest, the selectivity, can be determined.

It has also been plotted the SO_2 in front of % in the figure 18.

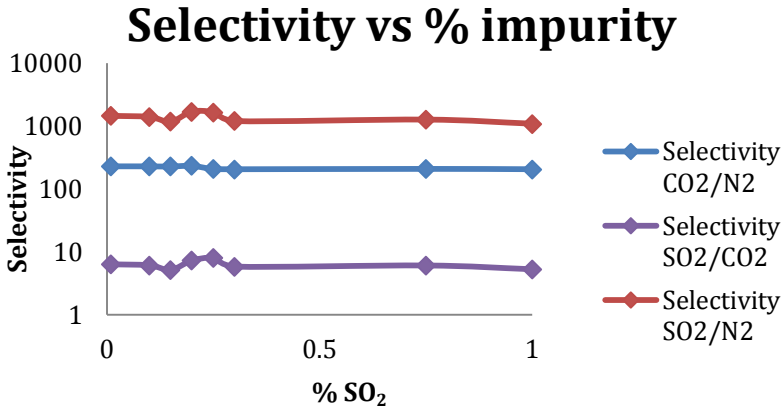


Figure 18. Selectivity vs % SO_2 impurity

Selectivity is a concept used as indicator to know whether a species has a higher tendency to be adsorbed than another. The larger is the value of selectivity, the sharper is the difference between the adsorption of an element versus another one. Therefore in the figure 18 we notice that SO_2 has got a higher selectivity than CO_2 , which, although is significantly higher, it has nothing to do with the difference that there is between the CO_2 and the SO_2 with respect to N_2 . Moreover, the SO_2 has got a selectivity factor over CO_2 around ten, and obviously, if we look at the graph, the difference between the selectivity of CO_2 and SO_2 with respect to N_2 , even being both of them really high, it is of a factor of 10.

6.3.2 Ternary mixtures including NO as impurity

In the same conditions as in the previous mixture, simulations have been realized in order to evaluate how adsorption of CO_2 is affected in terms of the increment of the NO proportion in the mix. The results obtained are shown in figure 19.

q ads vs % impurity

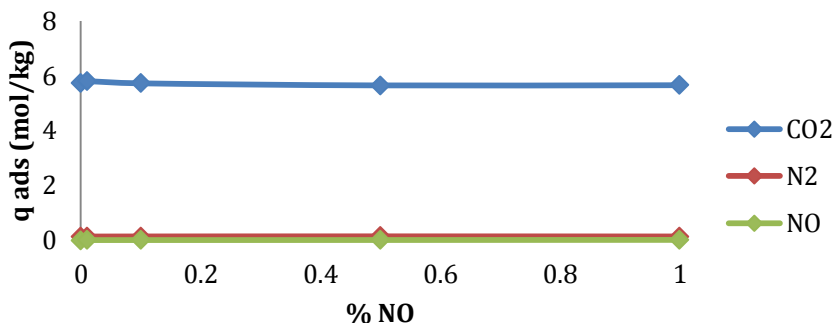


Figure 19. q ads vs % NO impurity

It can be noticed an abysmal difference with respect to the graph obtained in the mix with SO₂. The presence of NO in the ternary mixture has a nearly anecdotic effect in the adsorption process. This is due to the fact that, although apart from SO₂ it is the most adsorbed species of all the studied here by the MOF at pure conditions, it is of a magnitude degree very close to the one of the N₂, really far from the values obtain with CO₂ and SO₂. Thus it can be considered that the presence of NO does not affect in real terms neither the adsorption process of the system, nor the yield of CO₂ adsorption.

The quantity of CO₂ adsorbed in a pure flow at a pressure of 0.15 atm and 313 K is 6.11 mol/kg. This quantity is reduced to 5.73 mol/kg in the binary mix and at 5.64 in presence of 1% of NO. So it can be considered that the NO impurity does not poisons and that the most part of the adsorbed CO₂ lost, comes from the high proportion of N₂ in the gases mixture. In the table 5 are shown the quantities adsorbed by each element for the pure simulation (0.8 atm for the N₂, 0.15 atm for CO₂ and 0.01 atm for the NO), for the binary mixture (P total of 1 atm (0.85 N₂ and 0,15 CO₂)) and for the ternary mix with 1% of impurities, also at 1 atm of total pressure.

Table 5. Comparative adsorptions (NO impurity)

	q ads (mol/kg)		
	Pure	Binary Mix	Tertiary Mix (1% NO)
CO ₂	6.11	5.73	5.64
N ₂	0.28	0.14	0.12
NO	0.0085	-	0.013

From this information some hypothesis can be formulated about how the binary system N_2/CO_2 would evolve, with the addition of small percentages of other elements from which simulations for pure flows have been carried out. The simulations of these mixes have been beyond the established limits of this work. But we can expect that being the adsorptions of NO_2 and O_2 lower than the NO adsorptions, their presence at these percentages to be even less significant. And therefore, the only impurity that can become a problem to consider is the SO_2 . Even though, it is necessary to keep investigating and to carry out the proper simulations in order to confirm this fact.

Following the same procedure as before, a graph of the selectivity has been obtained (see figure 20)

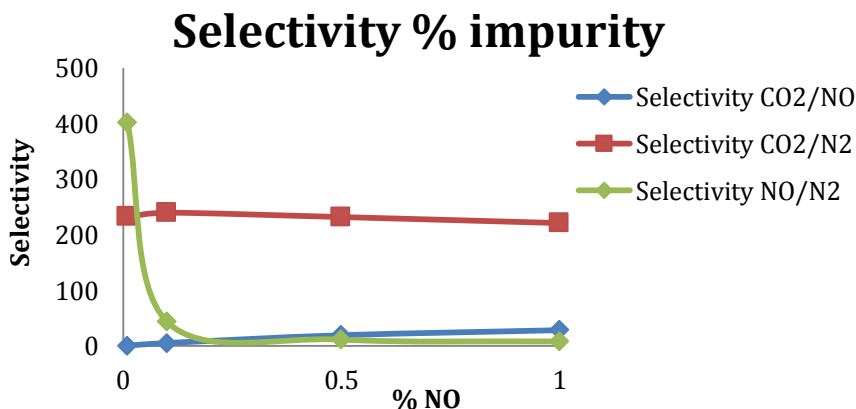


Figure 20. Selectivity vs % NO impurity

It can be perfectly noticed how the Mg-MOF-74 is very selective in favor to CO_2 , and it inclines for the adsorption of this specie instead of the NO or N_2 . Afterwards, the highest selectivity is the one of the CO_2 versus the NO , which, although it is at a much lower scale, gives selectivity values of 28 with presence of 1% of impurity of the mix. The MOF is also more selective for the NO than for the N_2 , although not in a so marked way. Even though in the graph the serial presence of selectivity of CO_2 versus N_2 is so high that detracts the abscissa axes and that differences are not well appreciated (the purpose of the graph is to give a more qualitative idea, rather than a quantitative one of the process), the selectivity values of NO/N_2 are around ten with 1% of impurity. It is, less than the half of the CO_2/NO selectivity.

It remains to say that NO does not mean a serious problem in the separation of CO₂ through Mg-MOF-74.

6.4 Swing Adsorption process

For the same gas mixtures, we have studied three different types of regeneration processes for the Mg-MOF-74, and it has been evaluated their associated energetic cost. These processes include TSA, in which heat is contributed to the system in order to release the adsorbed molecules, and the PSA and the VSA, where it is dealt with pressures and they are reduced in order to achieve the regeneration of the adsorbent material (see chapter 2.5).

For both mixes, the TSA evaluation has been carried out at two different temperatures, at 383K and at 443K, and considering that the temperature of entrance is at 313K. The VSA has been evaluated at two different pressure values as well, it is, taking the system to 0.1 and 0.05 atm respectively in order to carry out the desorption, and considering that it comes from a system at 1 atm of pressure. The PSA, which consists on the compression of post combustion gases before the entrance at the adsorption chamber to enable later desorption at atmospheric pressure, has been evaluated at an entrance pressure of 10 atm.

The results of the working capacity obtained depending on the desorption process used, for different impurity percentages, are shown in the figure 21. The darkest columns and retraced in black correspond to the NO impurity, while the other ones correspond to the results reached for the SO₂ impurity.

As it can be appreciated that the Δq obtained for the NO are higher than the ones obtained for the SO₂, and this fact increasingly grows as the impurity percentage increases.

This fact implies that NO does not affect the total adsorption of CO₂ in the MOF as much as the SO₂ does, since it is adsorbed in lesser proportion.

It can be also noticed that the processes through which the higher Δq are obtained are the TSA at 443 K ones, followed by the PSA. From the other ones, although further from these two processes, the VSA at 0.05 stands out.

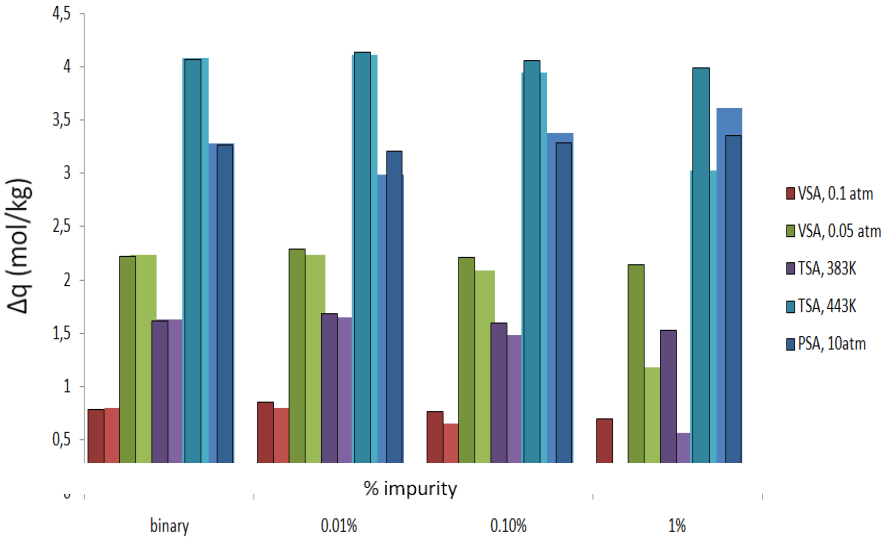


Figure 21. Working capacities at different processes and impurities

However the working capacity does not necessarily determines which is the best method, since each process has got associated an energetic cost, which may decant the balance towards one desorption process, even though it does not hold the highest working capacity value.

In this sense, the energetic index has been calculated for each process.

The evolution of required energy per quantity of CO_2 desorbed with the increase of the percentage in the mix of the impurity is shown in figures 22 and 23, either for the ternary mixture of SO_2 , as for the ternary mixture of the NO .

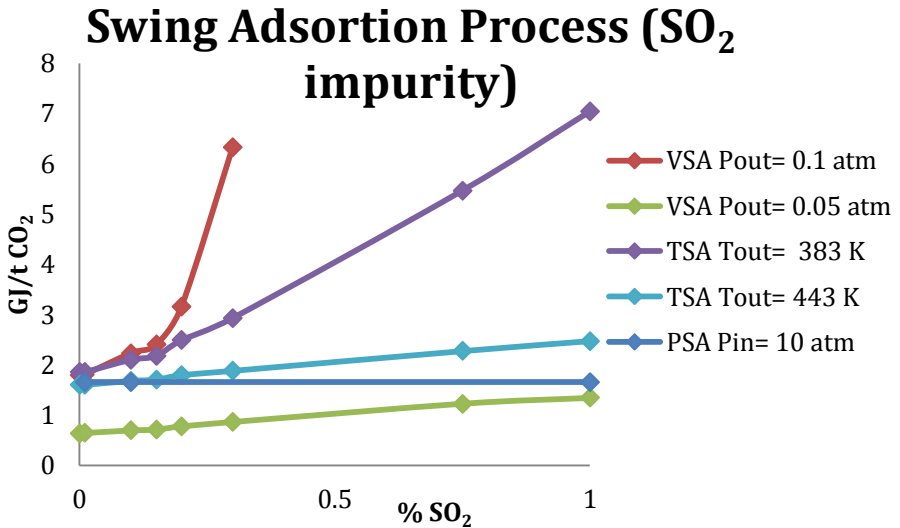


Figure 22. Swing Adsorption Process (SO₂ impurity)

From figure 22 we can conclude that the best option is the VSA at 0.05 atm, since it is the less energetic index option. However, it must be reminded that at industrial scale it is really hard to get to work at so low values of pressure, and therefore it may not be viable in some certain plants. The TSA option at 443K, and the PSA one at 10 atm are very similar at low impurities levels, but when these increase their presence in the mix, the PSA shows better results, since it keeps its energetic cost constant. Instead of that, the TSA at 443K increases a little the needed energy as the quantity of SO₂ in the mix increases.

On the other hand, it can be noticed that the reached results at low percentages are very similar for all the processes (only the VSA at 0.05 atm sticks out below the rest), and they are almost identical when there is not SO₂ in the system, so for the binary mix of CO₂ and N₂. However, as the presence of the impurity increases there are two processes which increase a lot the slope; the VSA at 0.1 atm and the TSA at 383 K. The TSA at 443K and the VSA at 0.05 atm increase at a much lower slope and they do it in a very similar way. Therefore the impurity affects them in the same manner, and the only difference is the ordinate at the origin, which makes that the VSA at 0.05 atm bears energetic costs (figure 23).

For the NO impurity the following results have been obtained:

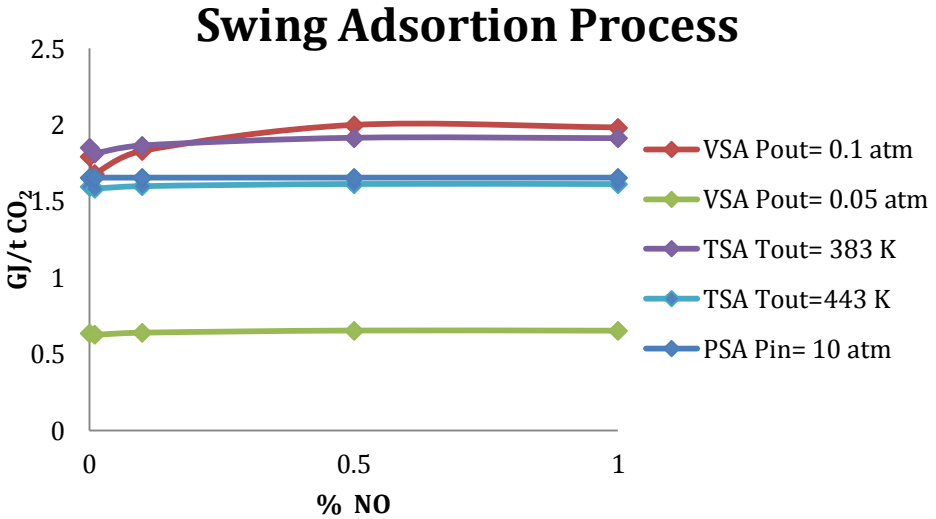


Figure 23. Swing Adsorption Process (NO impurity)

Taking a look at it, we realize that on the contrary to the graph obtained in the SO_2 , all the processes keep an almost constant energetic index with the increase of NO in the system. This fact must not disturb us, because if we analyze the graph of the q_{ads} versus the percentage of NO (figure 19), exposed previously, we realize that the quantity of CO_2 adsorbed is constant during the entire process. Thus the quantity of CO_2 to be desorbed does not show major variations with the presence of NO, and it makes sense that the regeneration processes occur in a constant way as well.

Once again the regeneration process with better results is the VSA at 0.05 atm, followed by the TSA at 443K. Therefore the VSA appears to be one of the best options, small variations in the pressure value when the system is depressurized alter a lot the results. In fact at 0.05 atm it is the best process among all the others, but instead, at 0.1 atm it situates in the last position. Thus, whether it is going to be implemented this mechanism in order to carry out the MOFs regeneration, it must be understood the need of being able to carry out depressurizations very close to the vacuum at industrial level. On the other hand, the TSA, which has obtained slightly lower results than the VSA, has got the advantage of being a system easy to apply at all the levels, since the heat contribution throughout heat exchangers has been studied in deep and it is already being carried out with assiduity in many industrial processes.

7. CONCLUSIONS

From this study focused on the adsorption of CO₂ in the Mg-MOF-74, several conclusions can be extracted.

- The forces field used for the description of the potential energy is correct, since the results obtained in the validation simulations properly adapts to the experimental values (extracted from the bibliography) obtained in the laboratory.
- The CO₂ adsorption capacity in a pure flow of the Mg-MOF-74 is very high. At a 0.15 atm pressure, which is the partial pressure that usually has the CO₂ in gaseous mixtures of post combustion, is 6.11 mol/kg. The rest of elements studied present, in pure flows, percentages of adsorption really lower than the CO₂, except from the SO₂, which is situated above and is the most adsorbed specie by the MOF.
- The ternary mixtures composed by 85% of N₂, 15% of CO₂ and the presence of the NO impurity, does not imply any problem with respect to the CO₂ adsorption. In spite of that, when the impurity is the SO₂, this specie strongly competes for the adsorptive centers and reduces drastically the quantity of CO₂ adsorbed.
- The TSA at 443 K is the process that enables to operate at higher working capacity levels, followed by the PSA with a gases compression at 10 atm previous to the entrance to the adsorption chamber.
- The regeneration method of the adsorbent with lower energetic cost is the VSA at 0.05 atm, followed by the PSA (P_{in} 10 atm), and the TSA at 443K. The PSA remains constant with the impurities percentage increase in the mixture, while the other ones are affected and increase the energetic cost index with the current impurity quantity.

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ACRONYMS

MOFs	Metal Organic Frameworks
q ads	Amount adsorbed (mol/kg)
q des	Amount desorbed (mol/kg)
PSA	Pressure Swing Adsorption
VSA	Vacuum Swing Adsorption
TSA	Temperature Swing Adsorption
Δq	Working capacity (mol/kg)
Q _{st}	Isosteric heat of adsorption (kJ/mol)
S _{ij}	Selectivity from <i>i</i> vs <i>j</i>
P	Pressure (atm)
T	Temperature (K)
MD	Molecular Dynamics
MC	MonteCarlo
U _{ij}	Potential energy between a pair of atoms <i>i</i> and <i>j</i> (kJ/mol)
U	Total potential energy of a system, or of an isolated guest molecule (kJ/mol)
x ₁	Mole fraction of a component in the adsorbed phase
y ₁	Mole fraction of a component in the gas phase
r _{ij}	Distance between two atoms, <i>i</i> and <i>j</i>
LJ	Lennard-Jones
e	Voidage of bed
e _{LJ}	Lennard-Jones depth of the potential well (kJ/mol)
η	Feeding/vacuum blower efficiency
σ _{ij}	Lennard-Jones potential diameter (m)

k	Polytropic parameter of gases
ρ	Framework density (kg/m^3)
R	Gas constant ($8.314 \text{ kPa m}^3/\text{kmol K}$)
Cp	Heat Capacity (J/kg K)

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APPENDICES

APPENDIX 1: LANGMUIR SETTINGS

For the accomplishment of the Langmuir settings, several linearizations can be used. From the typical Langmuir equation:

$$q = \frac{q_{sat} \cdot (b)P}{1+(b)P}$$

For the linearization of the pure isotherms of CO₂ and SO₂, the linearization that has achieved a better result has been the representation of P/q versus P. Therefore the equation of the line is:

$$\frac{P}{q} = \frac{1}{q_{sat} (b)} + \frac{P}{q_{sat}}$$

Langmuir setting to CO₂

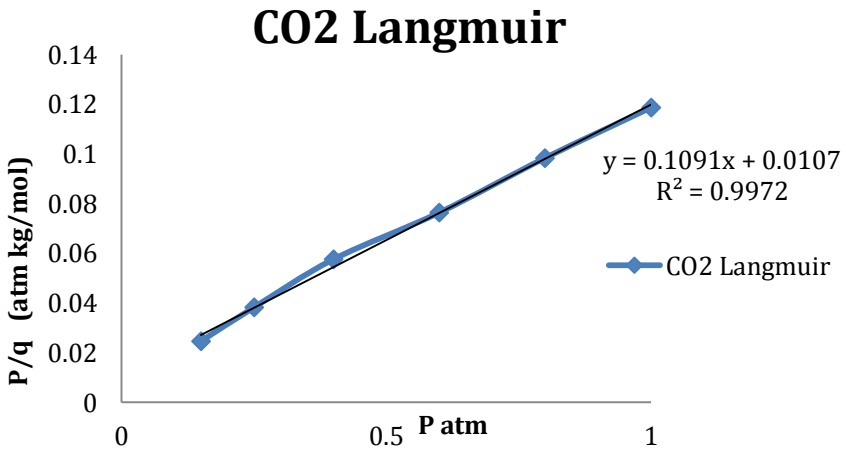


Figure A1. Langmuir setting to CO₂

Langmuir setting to SO₂

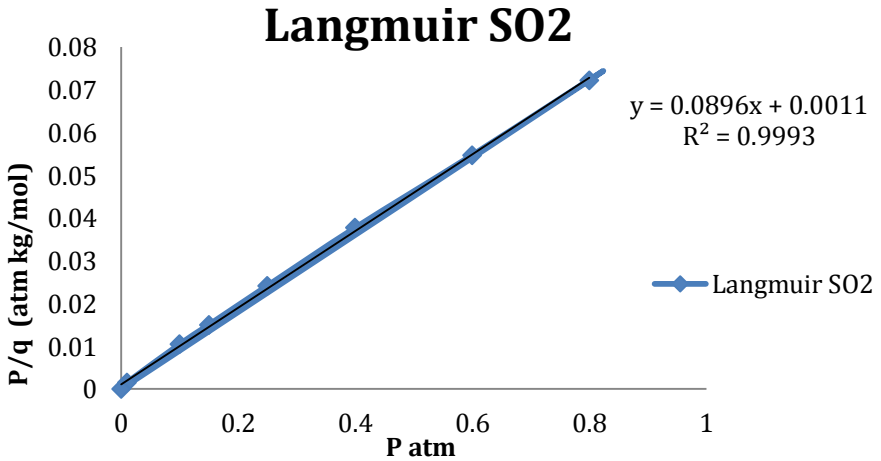


Figure A2. Langmuir setting to SO₂

Constants b and q_{sat} can be obtained from the slope and the ordinate at the origin of the equation of the line. The achieved values for each component, as well as the R , are shown in the table below.

Table A1. Langmuir parameters

	CO ₂	SO ₂
q_{sat} (mol/kg)	9.74	11.23
b (1/atm)	10.9	89
R²	0.997	0.999

APPENDIX 2: ESTIMATION OF THE NUMBER OF SIMULATION STEPS AT WHICH STABILITY IS REACHED

For each simulation undertaken, 1,000,000 MonteCarlo steps have been carried out. From which it has been considered that the first 500,00 are necessary to guarantee that the system is stabilized, and from the rest of steps a mean has been computed in order to obtain the final value from which all the graphs have been plotted and all the conclusions have been drawn. In order to yield liability to these words, it is shown below the graph in which it is represented the number of adsorbed molecules versus the number of steps done, either of pure CO₂ as of pure SO₂, at pressures of 0,01, 0,6 and 1 atm. It is clearly noticed that from the step 500,000, the system has reached an equilibrium. The graphs got for the rest of elements are of the same kind. They are not included in the appendices since their so low adsorption levels make it difficult to properly appreciate the oscillations between the steps.

In first place it is shown a graph obtained for the CO₂:

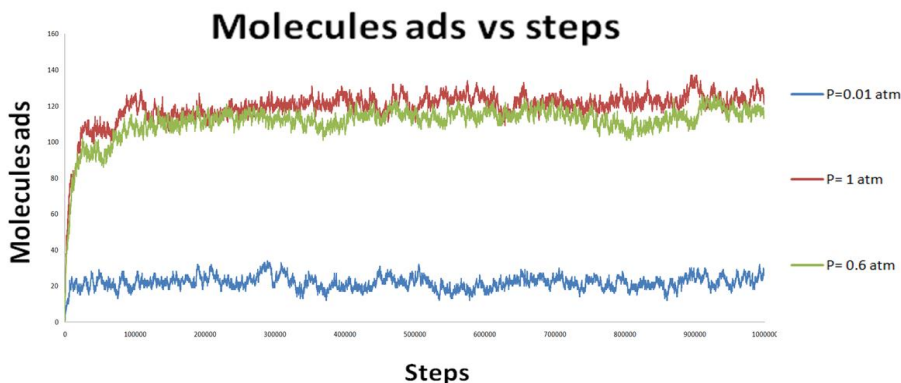


Figure A3. Molecules ads vs steps

In second place it is attached the graph obtained by SO_2

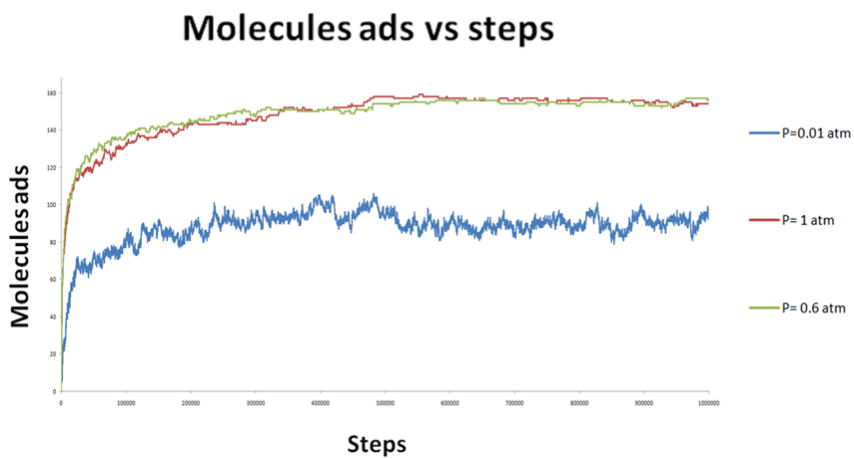


Figure A4. Molecules ads vs steps

