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Sorption of hydrogen chloride on solid sorbents

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I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

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Abstract

In recent years, the problem of chlorides removal in refineries has arisen. One of the refinery units which is mostly affected by untreated chlorides is the Continuous Catalytic Reforming Unit (CCR).

Under the operating conditions in the CCR reactor, organochlorides, which are continuously dosed to the catalyst for enhancing its activity, break down to HCl which is distributed in the fractionation unit between such streams as H_2, C_1-C_2, LPG and naphtha. If untreated, HCl flows through the refinery systems, causing various problems related to corrosion, poisoning of downstream catalysts, formation and deposition of NH_4Cl, etc.

Today there is a well established technology for HCl removal using adsorbents, these materials being able to effectively remove HCl. Nevertheless, the performance of HCl adsorbents has been found to vary from one CCR unit to another, the performance expressed in terms of products lifetime, capacity, operation conditions, byproduct formation, being quite different.

Because of the some uncertainty regarding the HCl adsorbents' performance, and considering the fact that the requirements related to the levels of HCl in refinery streams has become more rigorous, there is need to develop a methodology for adsorbents' testing. Therefore, the main goal of this project is to propose a methodology for in-house HCl adsorbents' testing that can not only help evaluating the performance of these solid materials, but also designing new, more promising adsorbents that can replace the existing ones in the nearest future.

The first part of this report represents a literature review focused on presenting the main problems caused by HCl in a refinery, theoretical concepts behind the adsorption process, but also the main adsorbent materials used in HCl removal units.

Further, the experimental setup used for testing of two commercial alumina-based adsorbents is presented. Besides this, the report contains a short description of the performed experiments and a discussion on the results regarding the adsorption of HCl on the two commercial adsorbents.

By performing experiments with HCl adsorption on two different adsorbents, it has been concluded that the methodology proposed for adsorbent's testing can provide with constructive results. This methodology makes it possible identifying with a quite high probability the mechanisms driving the overall adsorption process and quantifying the share of each mechanism. Moreover, it was possible to calculate the effective HCl removal capacity (breakthrough capacity) of the adsorbents - a key parameter in performance analysis of these materials. Last but not least, considering the fact that no kinetic analysis was included in the

described methodology, the latter was even found to be somewhat effective in identifying the possible mass transfer limitations that can affect the overall adsorption process.

Nevertheless, the methodology proposed in this report has space for improvement and some suggestions on this has been made in the last part of the report.

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Dedication

To my lovely parents, Vladimir and Galina Paereli.

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1 Introduction

Chlorides are chemical compounds containing chlorine. Some of them can be produced naturally, for example NaCl (halite), KCl (sylvite), $MgCl_2$ (bischofite), HCl, dioxins and many others, while the most are obtained synthetically - HCl, CH_3Cl, CCl_4, PVC, dioxins, etc. Chlorine containing compounds can be notionally divided into two big groups - inorganic chlorides and organic chlorides, each of them including both innocent and harmful chemical compounds.

One of the most known and used chlorides is hydrogen chloride (HCl). In normal conditions HCl is a colorless gas with a pungent odor. It is mostly used in the hydrochloric acid production, but also in production of vinyl and alkyl chlorides [1], in rubber hydrochlorination [2], petroleum wells activation [3] and even as catalyst additive (in Catalytic Reforming) [4,5]. However, in some industrial processes HCl appears to be byproduct (chlorination reactions, incineration of chlorinated organic waste) or even contaminant (in Catalytic Reforming) [6].

Refineries and implicitly refinery operators are experiencing nowadays significant problems with regard to hydrocarbons contamination, this issue becoming more and more actual and challenging if considering the continuous industrial growth, market evolution and, last but not least, the new environmental regulations [7]. The contamination of different refinery streams can lead to the well-known, worldwide experienced problems , such as: depositions on refinery equipment, plugging of the systems, deactivation of the catalysts and others. These effects can be more or less dramatic, so that in some cases the problem can be anticipated or eliminated relatively easily. For instance depositions on industrial equipment can be reduced by using filters for particles, additives for preventing their accumulation or simply by controlling the thermodynamics of the process. In this way, wax depositions can be eliminated by either using dispersants or controlling the temperature/pressure [8], while the formation of ammonia chloride in different systems is usually performed by dozing additives in hydrocarbon streams or by controlling the temperature along the lines [9]. Most of the contaminants, however, are usually removed from different refinery streams, this being done by adsorption, absorption, distillation or other physical, chemical or physicochemical methods.

One of the problems regarding hydrocarbons contamination in refineries is the removal of HCl from various refinery streams, such as H_2, LPG, naphtha, etc. [6,10] The problem has gained increased attention over the last decades and finding a solution has been an important milestone for the operators.

In this master thesis the adsorption of hydrogen chloride on solid sorbents is emphasized. The work aims to provide a method for adsorbent testing, this being an important step in both evaluating the performance of these materials, understanding the mechanisms of the process, but also in the formulating new materials with superior characteristics.

2 Overview of chlorides in a refinery

2.1 Sources of chlorides

Chlorides are present in crude oil in the form of both inorganic- and organo-chlorides. Prior to its processing, crude is undergoing desalination - an important process which aims to remove salts and water. Normally, most inorganic salts, including chlorides, are removed from crude oil at this stage. However, organochlorides, also known as "undesaltable chlorides", are impossible to remove in desalting vessels [11]. These compounds are therefore found in different concentrations in various crude fractions obtained upon petroleum distillation in the CDU (Crude Distillation Unit). During the processing of petroleum, organochlorides concentrate mainly in heavier oil fractions, but due to cracking processes, they also appear in lighter cuts. Some of these organochlorides are transformed into HCl (in catalytic reformers and hydrotreaters)[4,6] which is concentrated mainly in the lighter product fractions, such as off-gas (C_1-C_2 fraction), LPG and naphtha. Usually the concentration of HCl in these streams is quite small (4-40 ppm), yet it affects the system, making the removal of chlorides a crucial task [12].

Another source of HCl is the catalytic reforming catalyst itself. Catalyst used in this process has undergone many changes since 1949 when its first naphtha reforming "confrere" was formulated and patented by UOP [13]. The common characteristic of all catalytic reforming catalyst generations has been their bifunctional nature. The metal function is supplied by one or more metals (Pt, Re, Ge, Ir, Sn, In) deposited on a support while the acid function is provided by the support itself (usually alumina). In order to enhance its acidity, the support is chlorinated prior to impregnating the metal salts [5]. Thus, catalyst technology evolved from a monometallic Pt deposited on chloride alumina (Al_2O_3-Cl) catalyst to a trimetallic catalyst (e.g. Pt-Re-Ge/Al_2O_3) [14].

Due to the overall process technology change which have brought to life the Continuous-Regenerative Reforming (CCR), the modern catalyst support (usually ɣ-Al_2O_3) is continuously chlorinated for maintaining its acidity. Chloride ion is added to the support in the form of Cl_2 [4], HCl [5,14] or organic chlorides [6] which under the operating conditions break down to HCl and Cl_2. Because of a gradual slip of these components into the product streams, the latter become contaminated and the need of their efficient purification arises.

2.2 Problems caused by chlorides

Nowadays, refineries are extensive industrial complexes including a series of units for crudes separation and upgrading. With introduction of more severe product quality and environmental regulations, the challenges regarding oil processing have gradually increased. Hydrocarbon contamination problems have become an everyday challenge faced by the refinery operators and the solution everyone has been searching for could provide the key to a safer and more economic operation. The problem reviewed in this work refers to HCl contamination of refinery streams. The main issues induced by this contamination include: poisoning of the catalysts, increase in pressure drop over some units, corrosion of certain parts of the system, formation of green oils (see further), etc [6,10].

It has been reported [6] that HCl acts as a poison for Ni- and Pd-based catalysts. The problem has been related to poor removal of HCl from its mixture with H_2.

It is well known that catalytic reforming is one of the main "producers" of H_2 in a refinery. Some time ago when only topping and hydroskimming refineries were running, the problem was not regarded as being a severe one. These refineries were the simplest ones used in oil industry. Topping refinery was equipped with just atmospheric distillation unit (ADU), while the hydroskimming one included also the naphtha reforming unit and some hydrotreating units [15]. The consumption of hydrogen in these refineries was totally covered by its internal production (from the catalytic reformer) and its purity was at that moment not the major concern.

Nowadays, CCR is not capable of providing alone the necessary volumes of H_2 for covering the refinery necessities. Modern refineries are much more complex, having built in such units as hydrotreaters, operating in different conditions (from mild to severe), hydrocrackers, hydrogenation units, etc. These units are big "devourers" of H_2, so that the problem of producing as much and as pure H_2 as possible is a crucial task. In this way, for protecting the catalyst beds in hydrotreaters from being deactivated (poisoned) even traces of HCl from its mixture with H_2 should be eliminated.

When in combination with ammonia, HCl is transformed into ammonium chloride. The latter accumulates and deposits in the system, causing plugs which finally can lead to the shutdown of a whole operating units. The formation of NH_4Cl is a reversible process and is strongly dependent on temperature. Being an exothermic reaction (ΔH^0_f =-314.55 kJ/mol) [16], high temperatures shift the equilibrium towards reactants (HCl and NH_3). In this way, under the operating conditions of the catalytic reformer the formation and subsequent deposition of ammonium chloride is not an issue. However, in the downstream sections of the plant, where the temperature falls below 100°C, NH_4Cl remains stable and accumulates in the separation system, heat exchangers, compressors and pumps. Moreover, NH_4Cl was found to form a solid crust on the top of the chloride guard beds inducing also significant pressure drop over these [6].

One of the greatest problems regarding the presence of HCl in the system is related to its corrosive effects. Hydrogen chloride, as its name suggests, consists of an atom of hydrogen and one of chlorine which are connected by a covalent bond. The fact that Cl is more electronegative than H (H - 2.2, Cl - 3.16 on Pauling scale) [17] makes the H-Cl covalent bond quite polar. Therefore, the HCl molecule has a relatively large permanent dipole moment (1.12 D) [18], this in turn reflecting its high degree of solubility in water and other polar solvents. In contact with H_2O hydrogen chloride is forming H_3O^+ and Cl^-, the mixture being known as hydrochloric acid. Hydrochloric acid is a strong mineral acid and namely it is the one corroding different refinery systems.

The concentration of H_2O in light petroleum cuts is relatively very small, a fairly representative concentration being 15-20 ppmv [19]. However, this concentration appears to be high enough in order for hydrochloric acid to form in the system and thus cause severe problems in time. If not acting right and fast small problems can even turn into very costly shutdowns of entire units.

Another important problem caused by the presence of chlorides in the system is the formation of so-called "green oil". The formation of green oil is considered to be one of the most common problems associated with chloride guard beds [10,20]. These are long chain polymerized molecules formed by polymerization of organochlorinated compounds or co-polymerization of these with traces of unsaturated C_2-C_4 compounds in the presence of water. Polymerization takes place on the highly acidic surface of the sorbents and is promoted by the adsorbed HCl. It has been found [10] that beside the acidity of the surface and the presence of moisture, the formation of green oil is also dependent on the residence time. Having high boiling points and low viscosities, green oil can easily cause fouling and subsequent blocking of the equipment. Furthermore, in gas treating systems these compounds exhibit tendency to condensation, thus coating sorbents external surface and implicitly induce diffusion limitations. There was also observed and reported a significant reduction in the sorbents' lifetime [20].

The formation of green oil can be minimized or even avoided by using sorbents that form stable salts upon chlorides removal. In this case, chlorides removal is not anymore a physical process, but a chemical one in which a chemical reaction (usually irreversible) takes place on the surface of sorbents.

All the above mentioned problems related to the presence of HCl in different refinery streams have a high potential of influencing the operation and economics of a refinery unit (here mostly referred to CCR). Because of this, the necessity of developing a methodology for sorbents testing, understanding the effects of different parameters on the contaminant removal process, but also formulating new sorbents becomes the prior goal of the recent studies.

3 Theoretical concepts

3.1 Adsorption. Fundamentals.

Since many years ago scientists have come up with separation technologies. A good example could be the discovery of chemical elements. Many of the chemical elements known as of today do not exist as such in nature, but only in combinations or mixture with others. Thus, separation can be described as a transformation of a mixture of substances into two or more products with different compositions. There are many well-known separation processes today, for example distillation, adsorption, absorption, extraction, membrane-based technology, cryogenic processes, etc. for most of them separation being caused by a mass separating agent. For adsorption the mass separating agent is called adsorbent and so adsorption can be defined as transfer of material (adsorbate) from a fluid phase to the surface of a solid phase (adsorbent) [21].

Some of the separation processes mentioned above are opposite to "mixing" which is favored by the second law of thermodynamics [22]. Mixing, being a spontaneous process in these cases, is characterized by an increase in the system's entropy. Separation, on the other hand, is not spontaneous and, requiring external energy, many times it accounts for the major production costs in industrial units.

As distillation for example is opposite to mixing, adsorption is opposite to desorption. Both adsorption and desorption occur on the surface of an adsorbent and that is why these are called surface processes. Adsorbent's surface is represented by active sites that interact with solutes (ions, molecules) due to their steric and electronic properties. These active sites have different energies so that the adsorbent surface is energetically heterogeneous [23]. In order to enhance the adsorption, its driving mechanisms should be understood.

Separation based on adsorption is achieved by one of the following mechanisms: steric, kinetic and/or equilibrium effects [21,24].

Steric effect, also known as sieving effect, derives from the molecular sieving properties of molecular sieves and zeolites. This effect is unique with materials having well defined structures and reflects the ability of adsorbates to diffuse into the micro- and mesoporous framework of the adsorbent. In other words, the bulky molecules present in the system will not diffuse into the adsorbent pores, these being easy to access only for small and properly shaped molecules. Steric separation finds its applications in, for example, drying processes when using 3A zeolite or separation of normal paraffins from their iso- structures and other cyclic hydrocarbons using

5A zeolite [21]. These are the two largest applications of steric effect in separation technologies and are generally treated as equilibrium separations(see further).

Kinetic separation usually complements equilibrium separation and is used in cases when the latter is not feasible. This effect is unique by making possible separations driven by the relative diffusion rates of adsorbates. A typical example of kinetic effect is the separation of air into nitrogen and oxygen [25]. If air is to be separated by Pressure Swing Adsorption (PSA) using zeolites as adsorbents, the preferential adsorption of N_2 over O_2 occurs. If aiming to O_2 production and considering the fact that N_2 represents about 78% of the mixture, it is quite obvious that the energy needed for separation will be quite high. Instead, if using an adsorbent with a high selectivity for O_2 (the case of N_2 production form air), the energy required for separation can be reduced by as much as 3/4 if comparing to the previous case. Such an adsorbent can be for example a carbon molecular sieve (CMS). Although its adsorption capacity for both O_2 and N_2 is similar from the equilibrium point of view and represents only a fraction of that of zeolites, air separation (production of N_2) on CMS was found to be more economical. This phenomenon is attributed to the higher diffusion rate of O_2 in CMS, which is about 30 times the diffusion rate of N_2. The fact that the adsorption capacity of CMS for O_2 and N_2 is similar makes air separation by PSA possible only if the process cycles time are shorter than the typical ones. Otherwise, if the system is allowed to reach its equilibrium the separation fails. This fact emphasizes the complementary effect of kinetic separation to equilibrium separation.

Equilibrium separation is the driving force for most of the adsorption processes. The main characteristic of this separation is the establishment of a dynamic equilibrium between the adsorbate and the adsorbent surface. Dynamic equilibrium is represented by the number of adsorbed species on the surface and species desorbed from that surface. Equilibrium position in a system depends on the nature of different interactions between the adsorbate and adsorbent as well as on the strength of these interactions. Besides this, equilibrium is affected by such parameters as temperature, pH, existence of competing adsorbates, etc. For equilibrium separation to take place, a proper adsorbent should be selected, its properties being related to several fundamental properties of adsorbates [21]. Some of these properties that should be examined are: polarizability, permanent dipole moment, magnetic susceptibility, etc.

Polarizability is a property which describes the interactions between non-polar species and electrically charged species (ions, polar molecules). For a species with high polarizability to be adsorbed, such an adsorbent as activated carbon, which has hydrophobic surface area, can be used, while species having high permanent dipole moment will adsorb easily on highly polar surfaces of activated alumina and zeolites.

Adsorption equilibrium is established after a certain amount of species have "migrated" from the bulk phase onto the surface of the adsorbent and is determined by three variable: temperature, adsorbate concentration on the surface and adsorbent loading. Most of the times adsorption equilibrium is studied at constant temperature, adsorption being described through isotherms (fig. 1).

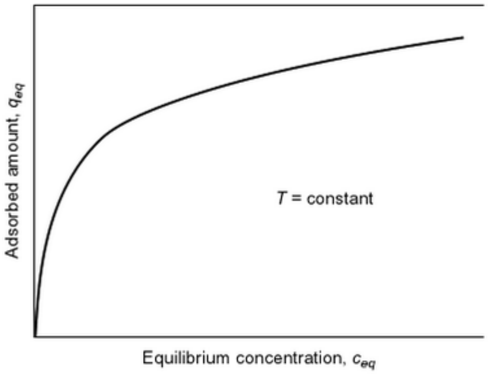


Figure 1: *Adsorption isotherm [23]*

All the above mentioned effects - steric, kinetic and equilibrium - constitute the driving force for separation processes based on adsorption and their understanding is crucial for the development of proper, highly efficient adsorbents. With the development of these adsorbents, adsorption processes will become more economic and efficient, being capable of withstanding even very difficult separations.

3.2 Adsorption isotherms

Adsorption processes are studied by using models. Each model can be described analytically (by a model equation) or graphically (by plotting the model equation). The result of plotting the model equation is known as adsorption isotherm (fig. 1).

Adsorption isotherm is represented by a curve and describes the relationship between the amount of a species adsorbed on the solid surface and pressure. As its name suggests, the variation in the amount of adsorbed species is studied at constant temperature.

As of today, more than 15 different adsorption isotherm models have been built. Among them, the most known are Freudlich-, Langmuir-, BET-, and Temkin adsorption isotherms. Further each of these models will be described shortly.

a) <u>Freundlich adsorption isotherm:</u> [26,27]

Freundlich adsorption isotherm represents the isothermal variation of the ratio of amount of adsorbate on the surface to unit mass of adsorbent with pressure. In 1909, Freundlich suggested an empirical expression for his model:

$$\frac{x}{m} = Kp^{1/n}\ , \tag{3.1}$$

where

x - amount of adsorbate

m - weight of adsorbent

p - equilibrium pressure of adsorbate

K, n - constants dependent on the adsorbent-adsorbate system and temperature

Experimentally it was determined that the amount of adsorbate on the adsorbent surface is directly proportional to the pressure in the system only until the saturation pressure is reached. Further increase in pressure does not affect the rate of adsorption which is in disagreement with Freundlich's model.

Freundlich adsorption isotherm is commonly used to describe the adsorption performance of heterogeneous surfaces, the model giving accurate results at low pressures.

b) Langmuir adsorption isotherm: [28,29]

Langmuir was the first to derive a scientifically based model. In 1918 he came up with a semi-empirical adsorption isotherm model developed from statistical thermodynamics. His model is based on four main assumptions:

- The adsorbent surface is uniform, so that the heat of adsorption is independent of surface coverage.

- During adsorption a single layer of adsorbed species is formed (monolayer adsorption), each active site adsorbing only one species.

- Adsorbed species do not interact and there are no phase transitions (immobile adsorption).

- Dynamic equilibrium between the gas phase and adsorbed species is established .

Langmuir isotherm describes the variation in adsorbent surface coverage with the pressure, the model being represented by the following mechanism and equation [30]:

$$\mathrm{A} + * \leftrightarrow A* \tag{3.2}$$

$$\theta = \frac{Kp}{1+Kp}\ , \tag{3.3}$$

where

A - a gas molecule (solute)

* - adsorption site

$A*$ - species A adsorbed on the adsorbent surface

θ - fraction of the adsorbent surface sites covered with species A

p - partial pressure of species A

K - adsorption equilibrium constant representing the ratio of rate constant of adsorption to the rate constant of desorption.

In most real cases adsorption does not fulfill the assumptions made by Langmuir because adsorbents surfaces are not perfectly flat (there are corrugation) and homogeneous, while adsorbed species are not inert. Moreover, most of the times adsorbed species form multiple layers on the adsorbent surface.

Despite its ideality, Langmuir model, which describes quantitatively the formation of a monolayer of adsorbed species onto the adsorbent surface, is well-known and commonly used due to its simplicity and capability to fit a variety of adsorption data.

c) <u>Brunauer-Emmett-Teller (BET) adsorption isotherm:</u> [31]

BET theory dates from 1938 when its developers extended the theory based on Langmuir concept. BET theory took into account multilayer adsorption while still assuming a physical character of adsorption of species on the surface. According to this theory, adsorption is followed by no interaction between the layers, the formation of these being consistent with the Langmuir theory assumptions.

Thus, BET mechanism can be represented as follows:

$$\mathrm{A} + * \leftrightarrow A* \tag{3.4}$$

$$\mathrm{A} + A* \leftrightarrow A_2* \tag{3.5}$$

$$\mathrm{A} + A_2* \leftrightarrow A_3*, \tag{3.6}$$

while the model is described by the following equation:

$$\frac{1}{v\left[\left(\frac{p_0}{p}\right)-1\right]}=\frac{c-1}{v_m c}\left(\frac{p}{p_0}\right)+\frac{1}{v_m c} \quad , \tag{3.7}$$

where

p - equilibrium pressure of adsorbate

p_0 - saturation pressure of adsorbate

v - amount of gas adsorbed

v_m - the amount of gas adsorbed corresponding to a monolayer

c - constant

BET model, developed for the characterization of gas-solid adsorption systems, is probably the most widely applied today. This model represents the basis of a characterization technique for porous materials, which involves the adsorption of N_2 on a solid surface at 77 K and a saturation pressure up to 101 kPa [32]. This technique is used to determine the surface area of a solid material, this area also being called BET surface area [30].

d) <u>Temkin adsorption isotherm:</u> [33]

The concept behind Temkin isotherm differs quite a lot from all the previously discussed models. This model was derived using statistical mechanics as a theoretical tool and it takes into account the adsorbent-adsorbate interactions [34]. It assumes that heat of adsorption is not constant, but varying linearly with surface coverage. This concept is widely accepted because such factors as the above mentioned adsorbent-adsorbate interactions as well as heterogeneity of the surface are considered to play an important role in adsorption.

Temkin model is represented by the following equation:

$$q_e=\frac{RT}{b}\,ln(AC_e) \quad , \tag{3.8}$$

where

q_e - the amount of gas adsorbed per gram of adsorbent (at equilibrium)

R - universal gas constant

T - absolute temperature

A, b - Temkin isotherm constants

In order to determine which model to use for describing the adsorption of certain species on a solid surface, experiments should be run. Once the adsorption experiments are done, isotherms can be plotted and conclusions regarding which model fits the experimental data best can be made.

3.3 Types of adsorption

Adsorption is by nature a surface phenomenon, its performance being strongly related to the unique properties of specifically designed sorbent material (adsorbent - in the case of adsorption). As mentioned previously, this phenomenon occurs when a species from a fluid phase approaches the vicinity of a solid surface, consequently undergoing an interaction with it. The nature of attractive forces created between adsorbent surface and adsorbate makes it possible to distinguish between different mechanisms which can lonely or conjunctively drive the process. Generally, adsorption is classified in physical adsorption (physisorption) and chemical adsorption (chemisorption) [35,36].

Physisorption is the type of adsorption described by weak intermolecular interactions, also known as Van der Waals forces, between adsorbate species and adsorbent. These interactions occur when the adsorbate approaches the solid surface.

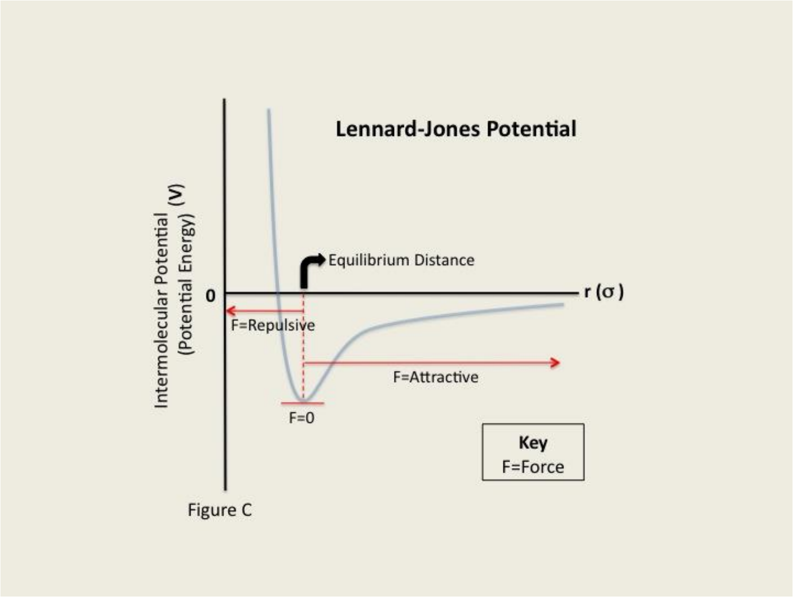


Figure 2: *Lennard-Jones potential energy diagram [37]*

Figure 2 depicts the potential energy diagram (Lennard-Jones potential diagram) which describes the variation of the potential energy of a species undergoing adsorption as a function of its distance from the solid surface of adsorbent . As a species is getting closer to the solid surface it begins to be attracted by the latter. These attractive forces bring the adsorbate species closer and closer to the surface until a certain distance, known as equilibrium distance, between the adsorbate and the solid surface is reached [37]. Equilibrium distance represents the maximum distance at which attractive forces between the adsorbate and the surface occur and the minimum distance at which repulsive forces between these two start to overcome. In this way the adsorbate becomes bound to the solid surface, its energy level being known as the adsorption (binding) energy. A distinctive feature of physisorption is that the adsorbed species is not fixed to the solid surface, but somewhat mobile, oscillating within the local minimum of the potential energy, region known as potential well. Physical adsorption is a reversible process and in order to desorb, the adsorbed species should overcome the attraction forces between itself and the solid surface. The required energy – desorption energy – equals to the energy of adsorption and can be provided for instance by increasing the temperature (thermal desorption) or reducing the pressure (see *Factors affecting adsorption*).

Physical adsorption takes place over the entire surface of the adsorbent, involving, under appropriate conditions of temperature and pressure, the formation of several molecular layers [31]. This process is exothermic but, because of weak interactions between the adsorbed species and the solid surface, the heat of adsorption is of the same order of magnitude as the heat of condensation – 10-40 kJ/mol [30].

In contrast to physisorption is chemisorption – a phenomenon involving a chemical reaction, thus characterized by the formation of a chemical bond between the adsorbate and the adsorbent surface. The process is exothermic and, as chemical bonds are stronger by nature than Van der Waals intermolecular forces, the heat of chemisorption is higher than that of physisorption. Typical values for heat of chemisorption lie in the range 50-400 kJ/mol [30], the released amount of heat being of the same order of magnitude as

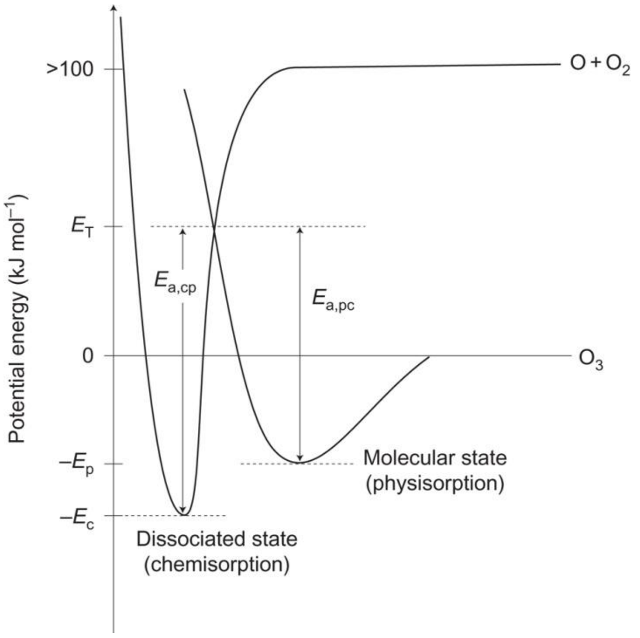


Figure 3: *Lennard-Jones potential energy diagram for the adsorption of* O_3 *[38]*

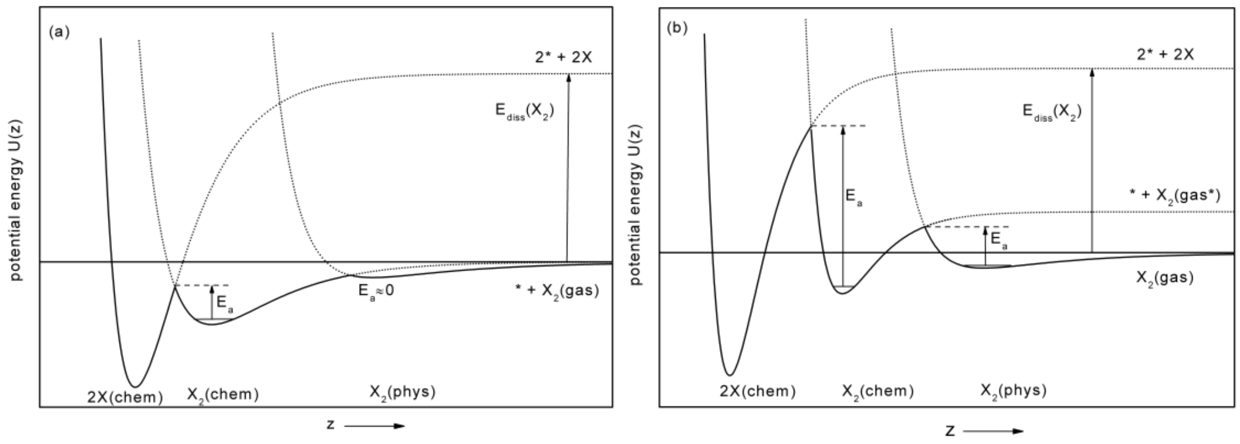


Figure 4: *Schematic representation of potential energy curves for a diatomic molecule (e.g. O_2) approaching a metal surface: non-activated chemisorption (left), activated chemisorption (right) [39]*

the change in the enthalpy of a chemical reaction.

In figure 3 is sketched a comparative potential energy diagram for a species undergoing physisorption and chemisorption. The physisorption takes place according to the mechanism described earlier. In order for chemisorption of a species to happen, this should first reach the equilibrium distance. At this point, if the species acquires a sufficient amount of energy, it can overcome the so-called activation barrier and, going through a transition state, enter into a dissociated state. It can be seen from the diagram that the minimum of the potential energy curve is "deeper" in the case of chemisorption, this being explained by a higher binding energy released upon adsorbate-adsorbent interaction [38]. Although one of the distinctive features of chemisorption is the need of activation energy, it is worth mentioning the fact that a species can go easily from a physisorbed state into the chemisorbed one without requiring high activation energy. The kinetics of the process depend very much on the point in the diagram where the physisorption curve crosses the chemisorption one (fig. 4). If the crossing point lies below the zero potential energy line then chemisorption is said to be non-activated (weakly activated) [39]. An example of non-activated chemisorption can be the adsorption of O_2 on most transition metals. Otherwise, the adsorption is called activated, so that in order to be chemisorbed a species should acquire a relatively high and sufficient amount of energy (activation energy). In the case of O_2 adsorption on Au, chemisorption is activated [39].

Unlike physisorption, chemical adsorption is a phenomenon which takes place over certain sites of the solid surface and involves only the formation of monolayer. Also, due to strong adsorbate-adsorbent surface bonds formed upon adsorption, desorption can be quite slow, in many cases the composition of desorbed species being different from the adsorbed ones. In order to desorb from the solid surface the adsorbate needs to acquire the desorption energy which is higher than the adsorption energy by exactly the amount equal to the heat of adsorption. Sometimes, when the bonds created between the solid surfaces and the adsorbate are very strong, chemisorption may be irreversible.

3.4 Factors affecting adsorption

Effect of temperature and pressure

a) Effect of pressure and temperature on system agitation

Adsorption is not an elementary process. This phenomenon, which involves the transfer of material from a bulk phase to the surface of a solid phase, comprises 3 steps: transport of the adsorbate from the bulk phase to the boundary layer - a thin film of fluid in the immediate vicinity of the solid surface [23,40], transport of the adsorbate across the boundary layer to the external surface of the adsorbent (including adsorption of the species) and, finally, its diffusion into the adsorbent pores (including adsorption of the species on the internal surface of the adsorbent).

Similar to chemical reaction kinetics, adsorption kinetics is very much influenced by the rate limiting step [41]. When a species from the bulk phase undergoes adsorption its motion can be subject to either diffusion limitations through the boundary layer (film diffusion) or diffusion limitations into the pore structure of the solid (internal diffusion). Usually the rate limiting step of adsorption is influenced by a parameter called agitation. When the system is highly agitated, internal diffusion might be the rate limiting step of the overall adsorption process (internal diffusion limitation is more sensitive to the adsorbent particle size), while film diffusion is the rate limiting step when the degree of agitation is low [42,43].

If adsorption process is described by a gas-solid system then for studying the effect of pressure on the degree of agitation the kinetic gas equation can be used [44]:

$$PV = \frac{1}{3}mnC^2 = \frac{1}{3}MC^2 \ , \tag{3.9}$$

where

P - pressure of gas

V - volume of gas

m - mass of one gas molecule

n - total number of molecules

C - root-mean-square velocity

M - mass of the gas.

Since the density of the gas can be expressed by

$$\rho = \frac{M}{V}\ , \tag{3.10}$$

the root-mean-square velocity will be:

$$C = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{\rho}} \tag{3.11}$$

As pressure is directly proportional to gas density (P/ρ=const. at a given temperature), it can be concluded that it does not affect the root-mean-square velocity, thus the motion of the gas molecules.

However, this is valid only for ideal gases. In reality, gases behave differently. If plotting PV against P (fig. 5), it can be concluded that the motion of gas molecules (their velocity) increases with pressure.

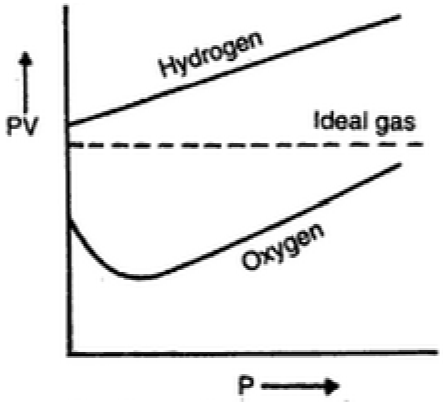


Figure 5: *The variation of PV with P for real gases [44]*

For evaluating the effect of temperature on the agitation, kinetic energy equation can be used [44]:

$$E_k = \frac{3}{2} kT \ , \tag{3.12}$$

where E_k - kinetic energy.

Considering the fact that kinetic energy is directly proportional to the square of the root-mean-square velocity, it can be concluded that an increase in temperature will lead to a faster motion of the gas molecules which, in turn, will result in an enhanced agitation.

b) Effect of pressure and temperature on adsorption kinetics

Pressure and temperature affect also the kinetics of adsorption.

Adsorption kinetics is described by the rate of gas molecules collision with the solid surface and the so-called sticking coefficient which represents the proportion of incident molecules which undergo adsorption [45]. The dynamic equilibrium can be described by the following equation:

$$A_{(g)} + * \leftrightarrow A* \ , \tag{3.13}$$

where

A - the adsorbate in gas phase

$*$ - available adsorption site

The rate of adsorption, similar to the rate of a chemical reaction, can be expressed in terms of the rate constant, the partial pressure of the adsorbate and the concentration of sites available for adsorption. Further, if writing the adsorption rate constant in Arrhenius form, the rate will be given by the following equation:

$$r_{ads} = Ae^{(-E_a/RT)} P^x C_\theta \ , \tag{3.14}$$

where

r_{ads} - rate of adsorption

A - pre-exponential (frequency) factor

E_a - activation energy (in case of physisorption E_a=0)

x - kinetic order

C_θ - the concentration

In order to consider the effect of the sticking coefficient on the rate of adsorption, the latter can be expressed in terms of the incident molar flux (F) and the sticking probability (S) [46]:

$$r_{ads} = FS \tag{3.15}$$

The flux of molecules undergoing adsorption can be written in term of gas pressure according to the Hertz-Knudsen equation [47]:

$$F = \frac{P}{(2\pi mkT)^{0.5}} \;, \tag{3.16}$$

where

k - Boltzmann's constant ($k=R/N_A$),

The sticking probability is a property of the adsorbent-adsorbate system which depends on two parameters: surface coverage (θ) and activation energy. This factor can be expressed by the following equation: [47,48]

$$S = f(\theta)e^{(-E_a/RT)} \tag{3.17}$$

Inserting (3.16) and (3.17) in (3.15) the final expression for the rate of adsorption is obtained:

$$r_{ads} = \frac{f(\theta)P}{(2\pi mkT)^{0.5}} e^{(-E_a/RT)} \tag{3.18}$$

Thus, it can be concluded that pressure has a positive effect on the adsorption kinetics (eq. 3.18).

The dependence of adsorption kinetics on temperature can be also formulated by using equation (3.18). Similar to pressure, temperature affects the rate of adsorption in a positive way, so that adsorption will occur faster if increasing the temperature. At the same time, temperature has a positive effect on the rate of diffusion (as mentioned earlier), this being explained by the fact that gas molecules move faster at higher temperature.

When chemisorption occurs on the adsorbents' surface an increase in temperature leads to an enhanced chemical reaction rate. According to the rate law, the reaction rate is proportional to the rate constant which is given by Arrhenius equation:

$$k = Ae^{-E_a/RT} \;, \tag{3.19}$$

where

k - rate constant.

So, as temperature increases the rate constant increases and consequently the rate of the reaction goes up.

However, the rate of adsorption will increase with temperature only up to a certain point when desorption(in case of physisorption) is favored thermodynamically or the equilibrium of the chemical reaction shifts in the opposite direction according to Le-Chatelier Principle(the case of reversible chemisorption).

c) Effect of temperature and pressure on adsorption thermodynamics

Besides influencing the kinetics of adsorption, temperature affects also the thermodynamics of the process. Adsorption is a spontaneous phenomenon, so it must be represented by a negative variation in the total free energy, also called Gibbs free energy [23,32]:

$$\Delta G_{ads.} = \Delta H_{ads.} - T\Delta S_{ads.} < 0\,, \tag{3.20}$$

where

$\Delta G_{ads.}$ - the variation in the Gibbs energy of the system

$\Delta H_{ads.}$ - variation in the adsorption enthalpy

$\Delta S_{ads.}$ - variation in the adsorption entropy.

In the bulk phase, a gas molecule has 6 degrees of freedom - 3 translation components, 2 rotation components and a vibration component. When this gas molecules is adsorbed on a solid surface it loses at least one degree of freedom (translational), this resulting in a negative variation of system's entropy [49]. Considering the above written condition ($\Delta G_{ads}<0$), it becomes obvious that the variation in the system enthalpy should be negative ($\Delta H_{ads}<0$). This fact implies that adsorption is an exothermic process which, in turn, means that adsorption is hindered when temperature increases.

If a reaction takes place on the surface of the adsorbent, then temperature will affect the thermodynamics of the chemical reaction. For example, when HCl reacts with a metal oxide impregnated on the surface of the solid material, heat is released because the reaction is exothermic. Nevertheless, the thermodynamics of the chemical reaction will be usually favorable ($\Delta G_{reaction}<0$) even at very high temperatures (700-750°C) [50], so that it can be concluded that temperature has a positive effect on the thermodynamics of chemisorption only up to the point when reaction reaches its equilibrium ($\Delta G_{reaction}=0$) (fig. 6)

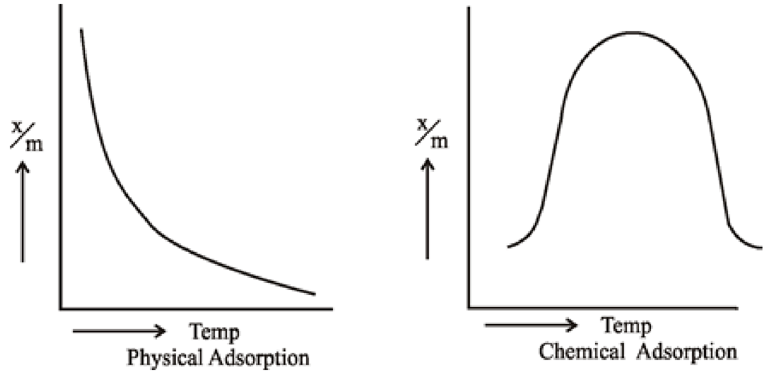


Figure 6: *Isobars describing the dependence of the amount of gas adsorbed on temperature (left - in case of physisorption; right - in case of a chemical reaction that takes place on the adsorbent surface)*

Adsorption thermodynamics is also affected by changes in pressure. If plotting an adsorption isotherm (fig.1), it could be seen that the amount of gas adsorbed on the solid surface increases with the pressure. This can be explained by the fact that pressure is directly proportional to the partial pressure of the adsorbate which consequently has a positive effect on the kinetics and thermodynamics of the adsorption process. However, the adsorption increases with pressure up to the point when pressure reaches the value of saturation pressure, i.e. when the surface is fully covered ($\theta=1$) by the adsorbate (the case of chemisorption). In the case of physisorption, when adsorption can occur in multiple layers, the amount of gas adsorbed will increase with pressure up to the point when the pores will be totally filled with the adsorbate.

Effect of adsorbent surface area and morphology

Besides the fact that adsorption is affected by temperature and pressure, this phenomenon is influenced by many other factors. As this process is described by a two-phase system (gas-solid or liquid-solid), the factors influencing adsorption can be classified in: factors related to the adsorbent characteristics and factors related to the adsorbate (or fluid phase) characteristics.

Among the most important factors that affect adsorption are the surface area and the morphology of the adsorbent particle. Adsorption, by nature, is a surface phenomenon, so the larger the surface area of the adsorbent particle, the greater the amount of adsorbed gas is (considering the gas-solid system) [30]. When preparing an adsorbent its surface area can be controlled in several ways, for instance by decreasing the grain size of the adsorbent particle or increasing the surface roughness.

Assuming that the adsorbent particle is sphere-shaped, it can be easily proved, by performing simple geometry calculations, that the surface area of a single spherical particle with a certain volume is lower than the sum of the surface areas of other two spherical particles with the total volume equal to the volume of the first particle. Nevertheless, it is the external surface area of an adsorbent particle that increases with decreasing its size, the internal surface area, which is usually much greater, remaining practically unchanged. Moreover, adsorbent particles are not perfectly sphere-shaped, there being many other shapes that producers have come up with over the years (fig. 7).

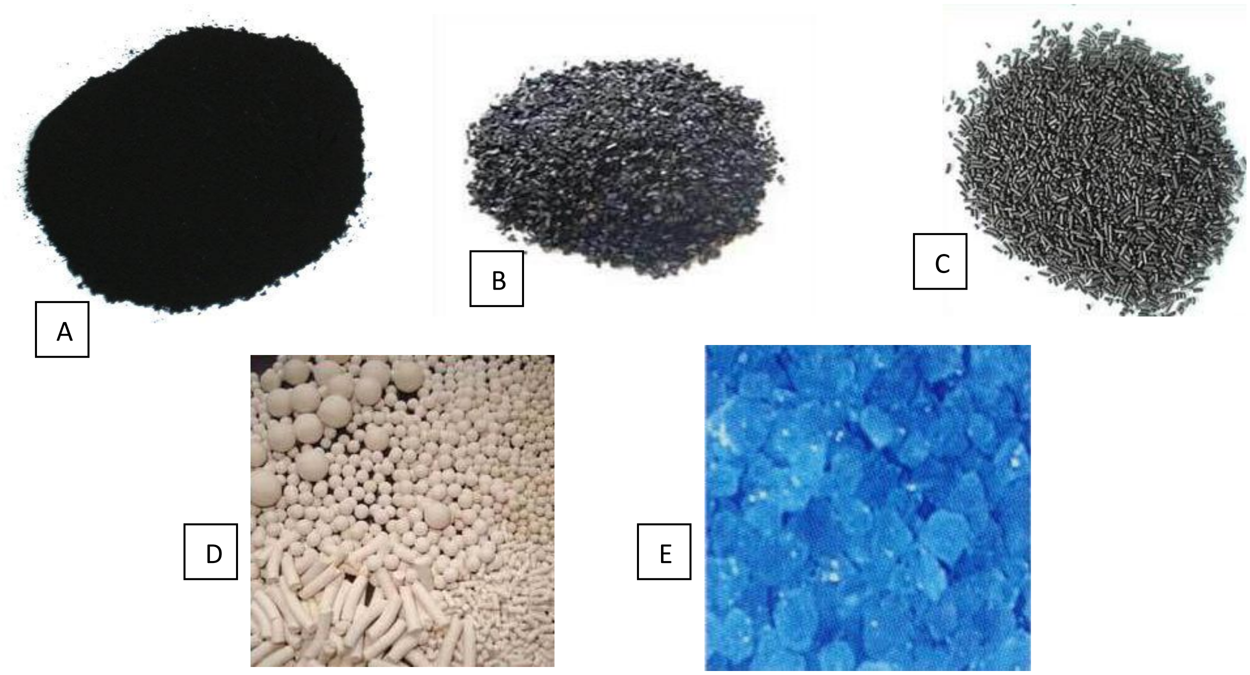


Figure 7: *Some example of adsorbents: activated carbon (powder) - A, activated carbon (granules) - B, carbon molecular sieve - C, molecular sieve type 13X - D, silica gel (granules) - E [51]*

However, particle size of a solid material can be lowered to a certain limit. When deciding on how small an adsorbent particle can be, one should make a trade-off between minimizing pressure drop across the adsorbent bed, minimizing internal diffusion limitations and ensuring a sufficient crush strength of the adsorbent [52]. For instance, if the diameter of the spherical adsorbent particle is small enough then indeed the mass transport limitation inside the particle is eliminated [53]. However, the pressure drop across an adsorbent bed formed of smaller particles is higher than in the case of particles with bigger diameter(size). Also, with decreasing the particle size of an adsorbent, its crush strength increases. Crush strength is an important property of adsorbents especially of those used in industrial applications and, in many cases, it plays an important role in the choice of adsorbent.

Surface area of an adsorbent particle can be increased also by increasing the particle surface roughness. The desired degree of the surface roughness can be achieved, for example, by mechanical rubbing of the surface, by chemical action or by depositing on the surface finely dispersed metal particles, this being done by either of the two most used techniques - electroplating or impregnation. It is though worth mentioning that if the degree of surface roughness is poorly controlled during the manufacturing process and, for example, an excessive deposition of metal particles on the solid surface takes place, the opposite effect can occur [54]. With increasing the plating time or the amount of impregnation material, the amount of metal deposited on the surface might increase to the point when, due to the pore blocking, the porosity and implicitly the surface area will be significantly affected in a bad way [55,56].

Usually, the surface area of an adsorbent is expressed in terms of specific area which is the surface area available for adsorption per either gram or unit volume of the solid. Specific area is considered to comprise two components: internal (greater) and external (smaller). According to Hodson, and Hochella and Banfield [57,58], the definitions of these two components of the specific area are "mathematically precise, but physically approximate".

Typically measured using the BET adsorption model, specific area, as explained earlier, indeed influences the adsorption process. However, if taking into consideration that adsorption can have either a physical, chemical or a mixed character, it should be remarked that the specific area influences directly the adsorption followed by the formation of a monolayer (could be physisorption or chemisorption). In contrast, physisorption accompanied by the formation of multiple layers, is more likely to be mostly influenced by the adsorbent pore volume.

Pore volume of an adsorbent particle is related to its property called porosity [23]:

$$\varphi = \frac{V_p}{V_T} \ , \tag{3.21}$$

where

φ - porosity

V_p - pore volume of the particle

V_T - total (bulk) volume of the particle.

As specific area, porosity is a very important characteristic of adsorbent materials. These can be classified in macroporous-, mesoporous- and microporous products, the last two being in particular interesting as adsorbents.

For instance, it is the porosity (microporosity and to some extent mesoporosity) of activated carbons (ACs) and activated carbon fibers (ACFs) that together with their specific area have made these materials be excellent adsorbents [59,60]. High porosity and very high specific area of these carbonaceous materials are achieved by subjecting the raw materials (wood, charcoal for ACs and carbon fibers (CFs) for ACF) to special treatment (activation). Activation could be done either physically, by subjecting raw materials to heat treatment under oxidizing atmosphere (e.g. CO_2, air, steam, etc.) or chemically, by treating these materials with activating agents as H_3PO_4, NaOH, HCl (see *Carbonaceous materials*).

Effect of the gas and adsorbate nature

By making the same assumption as previously, i.e. that the adsorption process is described by a gas-solid system, it is quite obvious that the phenomenon is influenced not only by the properties of the solid (adsorbent), but also gas characteristics (adsorbate).

As explained earlier, adsorption is a phenomenon which occurs due to appearance of attraction forces between the adsorbate and adsorbent. These forces can be weaker - of Van der Waals type - in the case of physisorption or stronger - chemical bonds - in the case of chemisorption.

In general, under certain conditions of temperature and pressure, the more easily liquefiable gases are adsorbed to a greater extent [61]. The ease of liquefaction is given by the critical temperature of the gas. Critical temperature is a physical property of a substance representing the minimum temperature above which gaseous substances cannot undergo liquefaction. This being said, it could be concluded that gases with higher critical temperatures are easily adsorbed on solid surfaces. By analyzing the problem deeper, the above mentioned fact can be explained by the stronger intermolecular (Van der Waals) forces of attraction in easily liquefiable gases [62].

However, it should be mentioned that the dependence of the amount of gas adsorbed on its nature is only valid for physisorption. Physical adsorption is non-specific by nature, so that under certain conditions of temperature and pressure, every gas is adsorbed to a certain extent on the solid surface.

In contrast, chemical adsorption is specific, which means that a gas molecule undergoes chemisorption only when a chemical bond between this molecule and the adsorbent surface is formed. For example, while being physisorbed at -190°C on Fe surface, N_2 does not adsorb in its molecular form on this surface at room temperature. This fact is apparent from the influence of temperature on the thermodynamics of physisorption but also from the fact that at room temperature no bonds are formed between the molecular N_2 and the solid surface of iron. However, it was reported [63,64] that at temperatures as high as 500°C N_2 undergoes chemisorption on Fe surface. This is explained exclusively by the dissociation of the N_2 molecule on the surface and formation of Fe-N chemical bonds.

It is worth mentioning that if the gas phase consists of a mixture of gases then adsorption is influenced also by the solubility of the adsorbate in the solvent. As solubility is inversely proportional to adsorption, the latter is hindered by strong solute-solvent interactions.

To summarize, there are many factors influencing the adsorption process. All the above mentioned properties of both the gas(adsorbate) and the adsorbent, as well as such factors as temperature and pressure have an effect on the efficiency of the phenomenon and it is important to emphasize that these factors does not act alone.

It is crucial to understand how such parameters as temperature and pressure affect both the thermodynamics and the kinetics of the process. In this way, by controlling their variation, but also the specific area, porosity of the adsorbent and other factors, the amount of adsorbed species and the rate of adsorption can be optimized, this leading to an increased efficiency of the adsorption process.

4 Adsorbents

Since adsorption has been first proposed as a separation technology, the concept behind this process has not known big changes. It is described by the same gas-solid or liquid-solid system in which interactions between the solid surface and certain species from the fluid bulk phase occur. However, there is a "part" of this technology that have changed over the years and this is the adsorbents.

Adsorbent technology for chlorides removal have experienced significant changes, these mainly being attributed to the introduction of new environmental regulations and product specifications. The development of new materials have aimed to improving their HCl removal capacity, selectivity and, last but not least, adsorbent's lifetime which is reflected in the change-out frequency of the adsorbent bed and, consequently, the economics of the process.

This chapter is based on a work with the title *Sorbents for chlorine and nitrogen compounds removal from LPG and naphtha.* This work, being a literature review, was written by myself and represented the specialization project within the Catalysis Group at NTNU.

In this chapter several sorbents are discussed. Their performance is evaluated in terms of such parameters as: operating temperature, adsorption capacity for HCl, selectivity (eventually the mechanism of HCl sorption will be discussed), regenerability and other.

4.1 Metal oxides

Metal carbonates, hydroxides and especially oxides have been used for a long time as sorbent materials for controlling acid gas emissions in gasification plants in combustion processes [50,65,66]. The most common compounds used in this sense had in their structure Ca^{2+}, Zn^{2+} and Mg^{2+}. Besides "dealing" very well with for example H_2S removal, these compounds were found to be quite efficient in HCl sorption.

Metal oxides (e.g. CaO, ZnO) can be prepared in different ways. Most common raw materials for their preparation are, in fact, their "confreres" - hydroxides and carbonates. For instance, CaO (quicklime) is obtained through dehydration of $Ca(OH)_2$ (slaked lime) at temperatures exceeding 400°C or calcination of $CaCO_3$ (limestone) at temperatures higher than 650°C. In both cases, it was observed and reported [66] that the prepared CaO has a higher surface area and porosity than its precursors and this is why among metal oxides, hydroxides and carbonates, the former are mostly preferred as sorbents.

Surface area, as discussed in the previous chapter is an important characteristic of sorbents. However, if compared to the specific area (surface area per gram or unit volume of sorbent) of other sorbent materials, CaO is far from being in the top (table 1). It was reported by Gullett et al. [66] that specific area of CaO lies in the range 5-40 m^2/g and that an increase in surface area can enhance the HCl adsorption capacity of CaO by up to 25%.

Table 1: *Specific surface area of some sorbent materials [33,66,68,69,70]*

Material	Specific surface area (m^2/g)
Activated carbon fibers	≈ 2000
Activated carbons	800-1500
Silica gel	300-600
Activated alumina	150-300
CaO	5-40

The same authors [66,67] have reported that if the sorbent particles are small enough (3-5 µm) then sorption of HCl on CaO is not affected in any way. However, as it should have been expected, an increase in particles size in the range 3-59 µm has a negative effect on the kinetics of the process (see *Factors affecting adsorption*).

Sorption of HCl on CaO has been found to involve a chemical reaction on the surface of the solid material [66,71], so that the process can be enhanced by either temperature rise or increase in reaction time. Reaction product, $CaCl_2$, was reported to be stable even at very high temperatures (700°C), the equilibrium concentration of HCl at 350°C being lower than 0.1 ppm. Thus, sorption of HCl on quicklime can be firmly considered irreversible. Gullett [66], Li [67] and Daoudi [72] found that HCl reaction with CaO is of first order, the activation energy lying in the range 22.2-31.1±3 kJ/mol. Performing experiments with mixtures of HCl and N_2 (Li et al., and Daoudi and Walters), and HCl and He (Gullett et al.), all have reported that the reaction between HCl and CaO is controlled by the external diffusion of HCl. This conclusion resulted from the fact that bulk diffusivity of HCl depends on the nature of carrier gas and is higher by a factor of 2.5 for the case of HCl/He system.

The performance of CaO as sorbent for HCl removal can be characterized as medium. The sorption capacity of this material is quite high, reaching values of 25-30 wt% HCl [10]. However, such high HCl pick-up levels were reported just in laboratory tests. Moreover, CaO can lower the concentration of HCl in a contaminated stream down to below 0.1 ppm. This high purification level, however, can be achieved only using big amounts of sorbent. Also, it should be noted that once CaO bed becomes saturated it cannot be regenerated, the sorbent material being discharged and replaced. This fact may affect the production rates and the economics of the adsorption process.

There is one more problem regarding the use of CaO as sorbent for HCl. For industrial application the crush strength of sorbent materials is sometimes the decisional factor when making a choice. In his work [73], Takase et al. have proved that due to the moisture present in the system $CaCl_2$ is deliquesced, fact that makes it soft and powdery. Because of this, the sorbent crush strength decreases drastically and the material should be replaced prior to its saturation. He found also that this problem can be solved by replacing CaO with ZnO.

CaO was found to sorb no or very little organochlorides [10]. In contrast, McWilliams et al. [74] have found that MgO have higher removal capacity for these compounds. He has reported higher breakthrough times for MgO in comparison with CaO and the ability of this sorbent to reduce the concentration of organochlorides to levels below 0.5 ppmw. The breakthrough time is defined as the time span between the start of the sorption and the point when the concentration of the contaminant in the outlet of the sorbent bed is higher than an imposed value. When speaking about HCl sorption, the breakthrough concentration is usually considered 1 ppm.

Even is the the sorption capacity of CaO is quite high, as mentioned earlier, the capacity of this sorbent corresponding the breakthrough concentration of 1 ppm is not higher than 1 wt%. Nor is it for ZnO and MgO. It is generally considered [75] that for being economically used in commercial applications a sorbent should have a retention capacity that exceeds 5 wt% of its weight. None of the above mentioned materials satisfy this notional condition and thus, to ensure high HCl removal efficiency, these sorbents should be used in quantities that exceed the stoichiometric ones by 2-3 times. In order to increase the efficiency of HCl sorption, metal oxides mixtures were tried.

To overcome the above mentioned limitations, Hue et al. [75] proposed a sorbent consisting of 20 wt% CaO, 53 wt% ZnO and powdered clay as binder. He has reported that this composite material is able to remove chlorinated compounds from a naphtha contaminated stream containing 40-60 ppmw chlorides, thus reducing their concentration down to below 1 ppmw. Moreover, the analysis have shown that the retention capacity of the prepared sorbent was 23.6 wt%, which is much higher than that of ZnO alone (0.96 wt%).

Another bimetallic sorbent was proposed and synthesized by Kameda et al. [76-79]. This sorbent consisted of Mg-Al mixed oxides and was prepared by calcining CO_3^{2-}-intercalated hydrotalcite-like compounds (CO_3^{2-} - HTs). HTs are layered double hydroxides (LDH), whose atomic structure is formed of positively charged octahedral layers of Mg^{2+} and Al^{3+} which are neutralized by an CO_3^{2-} interlayer.

The prepared sorbent was found to remove 95% of chlorides from a liquid feed at 30°C and almost all chlorides were removed only when the amount of sorbent used was 2.5 times the stoichiometric value. Same sorbent was tried in gas-solid systems (fig. 9) and the effect of water vapor on the sorption process was evaluated. It was reported that unlike in liquid-solid systems, in gaseous-solid ones HCl removal is not favored by high temperatures. This fact was found to be common for both wet and dry HCl systems. At the same time, the HCl removal efficiency of Mg-Al mixed oxide was proved to increase in the presence of H_2O at all the examined temperatures (130-190°C).

Two years later, Kameda et al. [78] found a new solution for treating gaseous feeds. In this sense, Mg-Al layered double hydroxide intercalated with CO_3^{2-} was used directly as adsorbent material. According to this concept, gaseous HCl reacts with CO_3·Mg-Al LDH producing Cl·Mg-Al LDH which subsequently undergoes ion exchange with CO_3^{2-}. In this way, the initial adsorbent is reformed and adsorption can continue (fig. 8). When using CO_3·Mg-Al LDH as adsorbent, no water is required for adsorption to be enhanced. The degree of HCl removal was reported to be higher than 98% for the stoichiometric amount of adsorbent and higher than 99% if its quantity is 1.75 times the stoichiometric value.

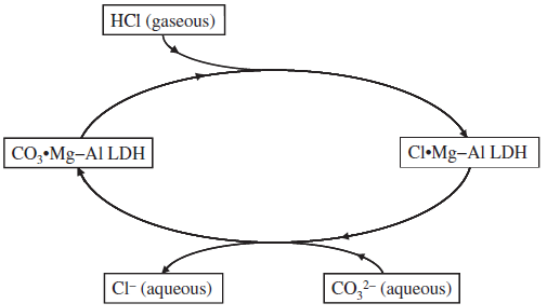


Figure 9: *Schematic representation of gaseous HCl removal using CO_3·Mg-Al LDH and regeneration of adsorbent [78]*

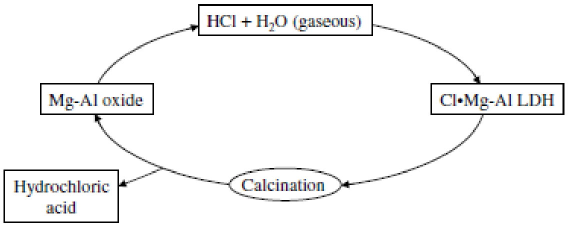


Figure 8: *Schematic representation of gaseous HCl removal using Mg-Al mixed oxide and regeneration of adsorbent [77]*

Conclusion:

Metal oxides and mixed metal oxides are materials that are able to remove chlorides from liquid, but especially gaseous contaminated streams. HCl is removed by reacting chemically with the solid material, the reaction being an irreversible one. Despite the fact that the kinetics of a chemical reaction is favored by higher temperatures, metal oxides were found to remove chlorides efficiently even at lower temperatures (<150°C).

The retention capacity of metal oxides for HCl, based on the breakthrough capacity of 1 ppm, is quite low (approximately 1 wt% of their weight) and not all of them are able to remove organochlorides. These limitations were overcome by the introduction of mixed metal oxides (Ca-Zn, Ca-Mg, Mg-Al) that have higher removal capacity for both HCl and organochlorides and higher lifetime (some of them being even regenerable (fig. 8, fig. 9).

Metal oxides and mixed metal oxides are non-acidic by nature, so these adsorbents have a very low tendency for green oil formation. These materials were found to be more efficient in single-phase systems with low space velocities and high concentrations of chlorides. Despite the fact that metal oxides can cope with both liquid- and gas-phase systems, their efficiency is somewhat lower in liquid-phase applications.

4.2 Activated alumina and promoted alumina

Activated alumina is widely used as substrate for catalysts and adsorbent. Among the most important applications of this material are: isomerization of n-butane [80], cracking of low-chain alkanes [81], dehydrochlorination of chloroalkanes [82], but also removal of fluoride, arsenic, selenium, beryllium and other natural organic matter from water.

When the problem regarding chlorides and especially HCl removal has arisen in refineries, activated alumina was regarded as a potential adsorbent in this sense and, in fact, was the first commercial available solution. The choice of researchers and refinery operators fell on this adsorbent mainly for two reasons.

First and foremost, activated alumina is a highly porous material with large surface area. At the same time, the mechanism of HCl adsorption on activated alumina relies also on chemisorption. Considering the synergetic effects of physisorption and chemisorption, alumina's surface area and morphology appears to play an important role in boosting adsorbent's capacity for HCl removal. Physical adsorption takes place due to interactions between the polar HCl molecule and polar sites on alumina surface (e.g. hydroxyl groups) [6]. However, there was found evidence [83] of HCl chemisorption on alumina surface, this occurring through two different

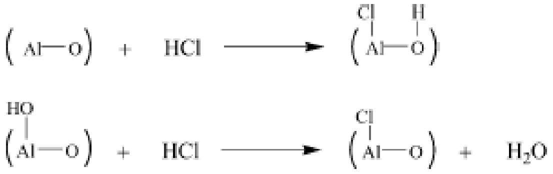


Figure 10: *Two routes of HCl adsorption on activated alumina [84]*

paths [84]: dissociation of HCl onto Al-O pairs with the formation of Al-Cl species and a new hydroxyl group and the dissociation of HCl on the Al-OH pairs with the formation of Al-Cl species and water (fig. 10). It has been reported [83] that the surface structure of alumina comprises four types of Lewis acid sites – weak, medium-weak, medium-strong and strong (fig.11) – and that the dissociative adsorption of HCl is mainly associated with the medium-strong ones (fig.12). It has been also reported [21] that hydrated surfaces of aluminas have also Brønsted acid sites (e.g. -OH groups). This type of acidity exists in ɣ- and η-alumina, whilst in θ- and δ-alumina, which are high-temperature phases, only Lewis acid sites (both tetrahedral and octahedral Al^{3+}) are found.

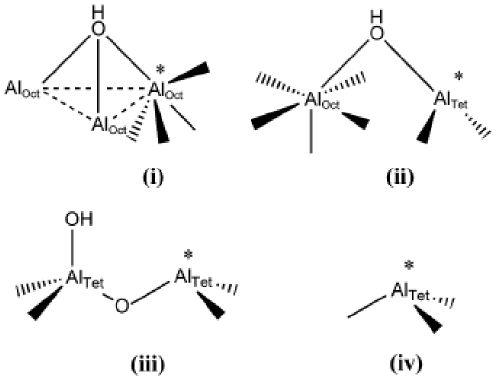


Figure 11: *Schematic representation of alumina acid sites. (i) weak Lewis acid sites, (ii) medium-weak Lewis acid sites, (iii) Medium-strong Lewis acid sites, (iv) strong Lewis acid sites. Asterisks indicate coordinative unsaturation. [83]*

Secondly, activated alumina was found to remove HCl from both gas and liquid contaminated streams. However, some authors [6] claim that this adsorbent is relatively ineffective in liquid phase applications. They reported that this behavior is mainly characteristic to liquid systems with low HCl levels, where the diffusion of the contaminant through the liquid film of adsorbed hydrocarbon compounds is hindered.

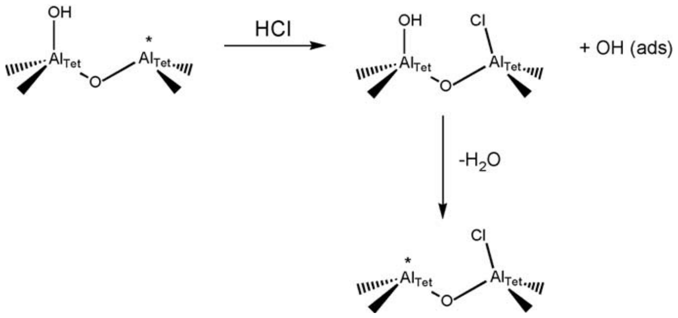


Figure 12: *Schematic representation of HCl chemisorption on medium-strong Lewis acid sites and the effect of subsequent water loss. [78]*

As HCl is removed by both physosorption and chemisorption on activated alumina surface, the overall process is favored by lower temperatures. At higher temperatures HCl will mostly chemisorb on the alumina surface and the theoretical capacity of the adsorbent will be reduced. At lower temperatures, physical adsorption interferes, this being highly influenced by the surface density of hydroxyl groups.

Unlike sorption on metal oxides, HCl adsorption on activated alumina is also strongly influenced by the presence of H_2O in the system. This can be simply explained by the fact that water molecule is polar, having a dipole moment even higher than HCl - 1.85 D (HCl dipole moment - 1.12 D [18]). This means that H_2O competes with HCl for adsorption on the active hydroxyl groups of the activated alumina surface.

Generally, activated alumina was found to have a moderate adsorption capacity for chlorides, this varying from 5-10 wt% of its weight [6,10]. The advantages of using this adsorbent for chlorides removal are the reversibility of adsorption, most of the HCl being removed by hot purging and the relatively low cost of activated alumina in comparison to other adsorbent materials used in this sense.

However, it should be mentioned that activated alumina has no or very low removal capacity for organochlorides and at the same time, being acidic by nature (fig. 11), exhibits relatively high tendency for green oil formation. Green oil is a mixture of long chain polymerized molecules formed by polymerization of organochlorinated compounds or co-polymerization of these with traces of unsaturated compounds. Its formation in the system can cause severe operational problems and even temporary shutdown of the unit. These major disadvantages of activated alumina were overcome by synthesizing and using as adsorbent promoted activated alumina.

Promoted activated alumina is a solid, high-surface-area material, prepared by impregnation of activated alumina with different amounts of alkaline or alkaline earth oxides [85]. Unlike adsorption on activated alumina, HCl adsorption on promoted activated alumina relies less on physisorption and more on chemisorption.

Physisorption of HCl takes place on the same surface hydroxyl groups of activated alumina, while chemisorption occurs on the surface of the promoters where usually an irreversible chemical reaction takes place. Promoted alumina can be used at higher temperatures since the share of chemisorption is much higher than in the case of activated alumina. Neverthelss, when used in low temperature applications, its adsorption capacity can be enhanced by preparing materials with high surface areas.

Over the years, the balance between physisorption and chemisorption in this technology have changed, the general chloride capacity derived from the balance of these two adsorption mechanisms being in the range 12-14 wt%. Moreover, chloride retention capacity of promoted activated alumina can be as high as 24 wt% of its weight [6], this level being reached by increasing the content of promoter. However, the other side of the coin is that these "super-promoted" products may lack high surface area and enough crush strength [86]. Because of this, the amount of metal oxides impregnated on the alumina surface should be strictly controlled in order for the final product to be used in industrial applications.

As in the case of activated alumina, promoted activated alumina can be used as adsorbent in both gaseous and liquid systems. Although the rate of liquid chlorides adsorption on promoted alumina is higher than on its "confrere" due to the high rates of irreversible chemical reaction that takes place, there are still diffusion limitations of the adsorbate through the liquid film formed on the solid surface [10].

Besides enhancing the overall chlorides retention capacity, promotion of activated alumina with metal oxides improved the performance of the former towards organochlorides. The ability of this adsorbent to remove some light organic chlorides together with its relatively low cost in comparison with other adsorbents places promoted activated alumina above its non-promoted homologue. However, promotion of activated alumina with metal oxides did not solve the problem of green oil formation, the tendency of this adsorbent towards formation on the adsorbent surface of polymerized long-chain hydrocarbons remaining relatively high. A solution to this problem was proposed by Blachman [86].

Blachman proposed an adsorbent based on alumina, impregnated with metal oxides and promoted with phosphates and/or organic amines. He aimed to obtain an HCl adsorbent that exhibits high retention capacity and, at the same time, has a reduced tendency to form green oil. Being strongly alkaline promoters, both phosphates and amines were expected to neutralize alumina's inherent surface acidity and implicitly reduce adsorbent's susceptibility to green oil formation.

Alumina substrate promoted with phosphates and/or organic amines proved to have higher removal efficiency for HCl, being able to reduce the concentration of the contaminant down to below 1 ppmv, and at the same time had almost no tendency to polymerization reactions. It has been reported that green oil formation is nearly suppressed by promoting activated alumina with diethanolamine (DEA), while its promotion with phosphates, Na_3PO_4 and K_3PO_4, increases the adsorbent retention capacity for chlorides. Besides this, the crush strength of prepared materials which contained up to 20 wt% of each promoter, the percentage being expressed as wt% on alumina substrate in the final product, was within admissible limits (more than 15 pounds for industrial applications).

Conclusion:

Alumina is a relatively cheap material with a moderate adsorption capacity for HCl. The biggest disadvantage of this adsorbent is it relatively high tendency towards green oil formation, which can subsequently lead to severe operational problems. Alumina has proved to be effective in both gas-solid and liquid-solid systems. However, due to the saturation of its surface with condensed hydrocarbons, which induces diffusion limitations, this material is not preferred in liquid phase applications, especially when the concentration of HCl is low.

Promoted alumina can be used at higher temperature, its adsorption capacity being enhanced by the metal oxides impregnated on the surface which react irreversibly with HCl. Since physisorption is almost suppressed, these materials are not regenerable which implies their dumping upon saturation.

Promotion with amines and phosphates can lower the acidity of alumina and therefore its tendency towards green oil formation.

4.3 Carbonaceous materials

Carbonaceous materials have gained popularity over the last decades. Among these are active carbons (ACs), carbon fibers (CFs) and active carbon fibers (ACFs), all having excellent adsorbing characteristics due to their unique properties (see further).

Active carbon, also known as activated charcoal, is a porous material usually found as powder or granules. It can be prepared from lignite, charcoal, petroleum coke or other inexpensive materials with low content of inorganics [87]. The choice of precursor as well as the fabrication method of active carbons are essential for obtaining a product with specific and desired properties.

When producing active carbon, first, the raw material is subjected to carbonization (pyrolysis under inert atmosphere). In this way, non-carbon elements are removed and a carbon skeleton with rudimentary structure is obtained. At the same time, carbonization leads to partial obstruction of carbon pores, so that one more step is needed in order to obtain a material with high porosity. This step is a crucial one in the formulation of final adsorbents and is called activation.

Carbon can be activated physically, by undergoing treatment with oxidizing gases such as CO_2, air or steam at temperatures as high as 800-1000°C, or chemically, by being treated with such activating agents as NaOH, H_3PO_4, HCl or other, under somewhat milder conditions (400-700°C) [27]. Chemical activation has proved to be more efficient, leading to the production of highly porous materials in a shorter time and, regardless of the fact that it is more expensive and implies the use of corrosive substances, this root is preferred.

Carbon fibers appeared on the markets in early 1960s. These materials were synthesized from cellulose fiber or phenolic/polyacrylonitrile resins. Even though these materials have been used in many areas (aeronautical, automobile, sports) due to their high chemical resistance, strength and stiffness, elasticity and low weight, their performance as adsorbents has not been reported. Instead, CFs were used as precursors for the production of ACFs (fig.13). For synthesizing ACFs, carbon fibers are subjected to heat treatment under oxidizing atmosphere at 700-1000°C [87,88]. In this way, materials with high porosity and extremely high surface areas (around 2000m^2/g) are obtained. These properties of ACFs have made them excellent adsorbents with wide applications.

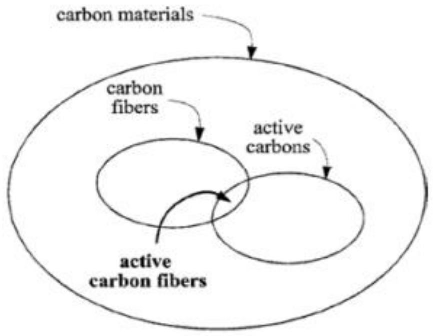


Figure 13: *Venn diagram showing the position of ACFs in the classification of carbon materials [87]*

As mentioned earlier in this report,both ACs and ACFs have various applications due to their high microporosity and high and extremely high specific surface areas. These materials have been tried also as adsorbents for HCl removal, but they are not known as being widely used in this sense at industrial scale.

Physical properties of these materials suggest that the main mechanism of removing such impurities as, for example, HCl is based on physisorption. Since physisorption, as its name suggests, is a physical process and the adsorption capacity is strongly dependent on the equilibrium established during adsorption of the contaminant on the solid surface, researchers have focused on modifying these materials, obtaining so-called supported or promoted materials.

Lee et al. [89] have prepared a supported AC by soaking it in a NaOH solution and controlled the loading of promoter on the surface by adjusting the soaking time. By passing a mixture of humid air and HCl through the adsorbent bed he has reported the formation of NaCl on the surface of AC. In this way, it was proved that besides physisorption, chemisorption plays an important role in the removal of contaminants from different gaseous streams. The removal efficiency of supported ACs was found to be 5 times the efficiency of original AC sample.

The mechanism of chemisorption is considered to consist of three steps: diffusion of HCl from the bulk phase to the pore mouth, further diffusion through the water film and dissolution in $NaOH_{(aq)}$ layer and, finally, reaction of the contaminant with the promoter. Since the original AC had a high surface area (1050m^2/g) which favored the good dispersion of NaOH on the surface, the diffusion path of HCl to the promoter was decreased. However, it was reported that the diffusion is hindered when not enough water is present in the system. This fact was explained by the formation and accumulation of NaCl in the adsorbent pores.

An important remark should be made regarding the concentration of HCl in the gas mixture. The concentration of HCl in the feed in the experiments performed by Lee et al. was 223000 ppm. Such a high concentration was used for reducing the test time. However, the behavior of the adsorbent might be different when the concentration of the contaminant in the feed stream is close to practical values (4-40 ppm). For instance, Fleming et al. [90] have reported that the capacity of an adsorbent can be dependent on the concentration of HCl in the feed stream.

The fact that the adsorption performance of ACs is improved by treating them with alkaline solutions was reported by many [55,91]. In his paper [55], Micoli et al. have modified ACs by impregnating them with NaOH, KOH and Na_2CO_3 (table 2).

Table 2: *Composition and surface area of commercial and modified active carbons [55]*

Sample	Preparation method	Active phase (mmoleq/g)	Surface area (m^2/g)
AC (RGM 3)	–	–	1110
AC-NaOH	NaOH impregnation	7.98	1039
AC-KOH	KOH impregnation	2.6	1322
AC-Na_2CO_3	Na_2CO_3 impregnation	5.01	1106

The efficiency of the prepared samples was evaluated in terms of breakthrough times. By passing a gaseous mixture of HCl and N_2 through the adsorbent bed, Micoli et al. have concluded that the AC sample impregnated with NaOH had the poorest efficiency, this being followed by the non-promoted AC sample, AC-KOH and AC-Na_2CO_3. It is worth mentioning that the breakthrough time of the sample impregnated with carbonate was 8 times larger than that of the sample impregnated with sodium hydroxide. Nevertheless, all the samples were able to reduce the concentration of the contaminant to below 1 ppm, the lower efficiency of the AC-NaOH being related to the very high content of the active phase on the surface (table 2) which led to pore occlusion.

Supported active carbons were found to be regenerable [89], this consisting in washing NaCl and eventually the unreacted promoter from the adsorbent surface with water or low pressure steam, drying the material and subsequently re-soak it in a alkaline solution.

The surface of both ACs and supported ACs are non acidic by nature and therefore these adsorbents does not favor the polymerization reactions of organochlorides which lead to the formation of green oil.

Unlike ACs, ACFs are, as such, less suitable for removing hydrophilic adsorbates from contaminated streams. This is due to the fact that these materials are synthesized from CFs, as mentioned earlier, at very high temperatures. The high degree of microporosity and mesoporosity of ACFs, as well as their extremely high surface area makes it possible, though, to remove contaminants by physisorption. However, the surface of these potential adsorbents is usually modified. There are many known methods for ACFs surface modification: mechanical treatment, chemical treatment, thermal treatment. However, plasma treatment is preferred because it excludes the formation of any chemical residue and does not perturb the bulk properties of the product [60].

Atmospheric plasma treatment is done in a reaction chamber (fig.14), in which N_2, O_2 or other gases, being dissolved in a carrier gas, pass through the inside of an electrode and then are sprayed over the ACF surface [92]. The presence of these hydrophilic nitrogen-rich, oxygen-rich and other surface functional groups makes it possible for ACFs to adsorb HCl. Some of these functional groups are alkaline in nature, others are acidic, so that the adsorption of HCl occurs through Lewis acid-base interactions.

Kim et al. [60] have treated a commercial sample of ACF having the specific area of 2121 m^2/g with N_2, O_2 and CO_2. Upon N_2 treatment, it was concluded that the carbon and oxygen content did not change, while the nitrogen content was almost doubled. Mostly C-N functional group was found on the surface, but also C=N and O-N.

When treating the sample with O_2, the content of carbon have decreased, the nitrogen content did not change, while the oxygen content increased more than the content of nitrogen in the previous case. The most abundant functional groups found on the ACF surface was -OH. Besides this, -C=O, O=C-O, -C-O- and even physisorbed oxygen were identified.

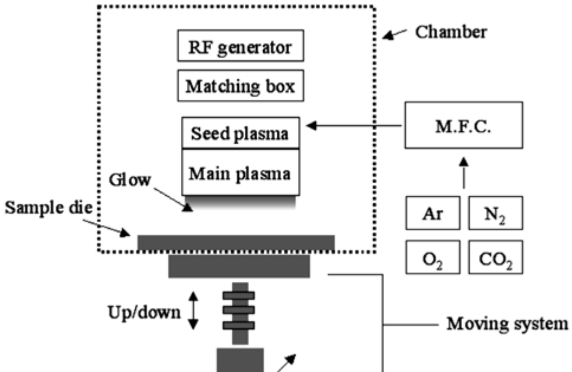


Figure 14: *Schematic representation of the atmospheric pressure plasma device [60]*

The treatment of the commercial ACF with CO_2 have led to the highest oxygen content and lowest carbon content if comparing to the previous two cases. Upon CO_2 treatment of the surface, mostly carboxylic and ester groups were identified on it.

When evaluating the acidity of the ACFs surface, Kim et al. have reported a higher surface acidity of the sample treated with CO_2 and the lowest surface acidity of that treated with N_2. This conclusion was totally assigned to the more alkaline nature of the nitrogen radicals formed on the surface and the more acidic nature of oxygen radicals. Also, the acidity of ACFs surface is thought to be dependent on the temperature used for their synthesis [93,94], so that ACFs prepared at higher temperature have more alkaline surfaces.

The basicity of the surface appeared to play an important role in the removal of HCl. Thus, the sample treated with N_2 have shown the highest performance, due to establishment of stronger Lewis acid-base interactions between the alkaline nitrogen functional groups and HCl.

However, even after modifying the surface of ACFs, the removal capacity of these materials is not that high, contaminants (in this case HCl) being removed mostly by physisorption and to some extent by Lewis acid-base interactions. For enhancing their performance, supported ACFs were prepared. By depositing Cu, Ag, Ni, nanoparticles on the surface of ACFs, materials with better HCl adsorption characteristics were obtained.

Park and Jin [54] have evaluated the performance of ACFs electroplated with Ag and compared it with the performance of a commercial ACF with the specific area of 2477 m^2/g and pore volume of 1.22 cm^3/g.

Despite the fact that upon electroplating the surface area and pore volume of the commercial sample decreased, the removal efficiency of the majority of prepared samples have increased substantially. By performing X-ray diffraction analysis, Park and Jin have reported the presence of AgCl on the surface of spent adsorbent, thus concluding that Ag nanoparticles act as active sites, allowing HCl not just physisorb on the adsorbent surface but also reacting with the promoter.

However, not all the prepared samples showed a better removal capacity for HCl. For instance, samples containing higher concentrations of Ag (more than 22 wt%) had an efficiency even lower than that of the commercial ACF. This fact was explained by a drastic decrease in the specific surface area upon electroplating (by a factor of 2) and significant reduction in the total pore volume (by more than 50%) caused by pores blocking. Thus, it was concluded that the concentration of the promoter, and implicitly electroplating time, should be carefully controlled.

In a further work [56], the synergetic effect of Ag and Ni on the ACFs surface was examined. The sorption performance of these bimetallic sorbents composed of Ag and Ni clusters have proved to be even higher that in the case of Ag/ACFs sample. In this way the share of physisorption have decreased even more, the adsorption of HCl on ACFs being mostly assigned to chemisorption.

However, as in the case of Ag electroplating, the excess of Ag and Ni on the ACFs surface have led to pore occlusion. Moreover, surface analysis have shown that when there is an excess of Ni, it covers Ag nanoparticles, subsequently prohibiting the co-reaction of the two metals with HCl.

Conclusion:

Active carbons and active carbon fibers are very promising adsorbents when referring to HCl removal from various contaminated streams. In order to ensure their high performance, an eye should be kept on the synthesis of these materials, especially on the activation/treatment stage. It is preferred that treatment is done at lower temperatures in order to maintain the bulk properties, especially the high porosity and the extremely high surface area, of the final products.

Removing HCl mainly by physisorption, the capacity of these materials can be improved by modifying their surface (plasma treatment) and/or by depositing on it active metals, hydroxides or carbonates. The higher the concentration of these substances on the surface, the larger the share of chemisorption is. However, the excess of active phase on the adsorbent surface leads to a dramatic decrease in the specific surface area of the material and its total pore volume.

All in all, by controlling the temperature during the preparation of ACs and ACFs, modifying the surface of these materials, thus making it more hydrophilic and, last but not least, by ensuring an uniform deposition of an active phase on their surface, highly efficient products can be obtained.

The only problem regarding these materials is there relatively high cost which does not make it possible to use them at industrial scale. Even so, their good performance appears encouraging and the finding of cheap and available precursors can open them the door to practical applications.

5 Fixed bed adsorption

For the experimental part, alumina has been chosen as adsorbent. This material is widely used in the industry, has a relatively high adsorption capacity and has a relatively low production cost.

By varying the parameters influencing the adsorption of alumina in a fixed bed column, the breakthrough curves were studied. The series of performed experiments made it possible to come with a methodology for adsorbents' testing, this making possible the evaluation of the material performance, understanding the mechanisms of the process, but also offered the possibility of formulating new materials in the future.

5.1 Background

Fixed bed adsorption processes are found everywhere in the chemical industry. Some of the applications include gas dehydration, air purification, water purification, contaminants removal from hydrocarbons. This separation technique is based on a solid material which is placed inside an adsorption column that aims to separate one or more components from a fluid phase passing through the packed bed.

The mechanism of adsorption relies on the diffusive properties of the sorbate from the fluid flow, the adsorption being controlled by both the diffusion of the contaminant through the thin film around the particle(external mass transport) and its subsequent diffusion into the material pores(internal mass transport) (fig.15) [95,96]. External diffusion of the adsorbate to the external surface of the solid depends mostly on the flow rate of the fluid(solute) through the fixed bed and the concentration of the solute, so that a higher flow rate and/or higher concentration of the solute reduces or even eliminates the external mass transfer limitations.

Internal diffusion of the adsorbate into the adsorbent pores is affected largely by size of the particle and, intrinsically the size and smoothness of the pores. When decreasing the size of the adsorbent particles, internal diffusion resistance also decreases which translates into an increased internal diffusion rate. Internal diffusion rate increases because the pathway of the solute to the internal surface of the solid material is shorter [53].

When either of the rates of diffusion is slower than the rate of adsorption, it can be said that adsorption is diffusion-limited and in order to quantify the effect of either of the mass transfer resistances, a detailed kinetic analysis should be performed.

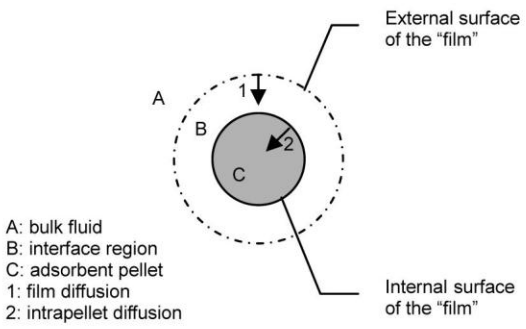


Figure 15: *Macroscopic adsorption process on an adsorbent pellet [95]*

Unlike in batch adsorption systems, experiments with fixed bed columns does not provide results regarding the shape of adsorption isotherms (see *Adsorption isotherms*). Instead, when performing adsorption experiments in fixed bed systems, the breakthrough curve of a solid material can be sketched, this, in turn, providing information on the real capacity of the adsorbent in time. Fixed bed systems could also provide information regarding the mechanism of adsorption and the regenerability of an adsorbent.

Performing experiments in fixed bed columns makes it possible to simulate better the conditions of an industrial adsorption process and this is why this system have been chosen for the experimental part of this work.

As mentioned earlier, the breakthrough curve provides information about the real capacity of the adsorbent and not just the equilibrium one. As the solute adsorbs onto the surface of the solid material, the latter starts to saturate, ensuring a very low concentration of the contaminant in the outlet of the bed. In time, adsorption zone moves through the column (fig.16) and when it reaches the bottom, breakthrough occurs. At this point the concentration of the solute starts to increase, approaching its concentration in the feed stream [97].

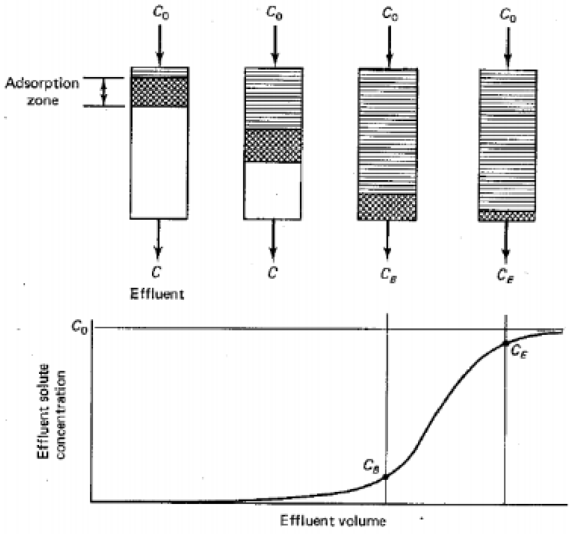


Figure 16: *Mass transfer zone in an adsorption column [97]*

An example of breakthrough curve is shown in figure 17. This S-shaped curve determines the breakthrough concentration of an adsorbent, its lifetime, as well as the regeneration time needed for a certain bed length.

The shape of the curve changes with changing the parameters of the process. Thus, being influenced by the feed flow rate, feed concentration, the type of adsorbent, its size and shape, the breakthrough curve can appear steeper or smoother, shorter or longer, and with a different breakthrough time. It is important to mention that the breakthrough concentration which denotes the starting point of the contaminant slip through the bed is normally chosen considering the desired purity of the effluent. In the case of HCl adsorption, very low concentration of this contaminant in the effluent is wanted, since even very small concentration of HCl in hydrocarbon streams can cause severe operational problems in an industrial unit (see *Problems caused by chlorides*). Because of this, for all the experiments performed, the breakthrough concentration was set to 1 ppm.

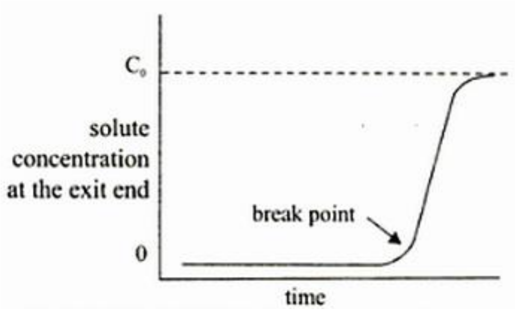


Figure 17: *Idealized breakthrough curve [30]*

5.2 Materials and samples preparation

For the experiments, four alumina-based adsorbents were used. Two of the samples with an unknown composition, further referred to as samples A and B were commercial adsorbents used at industrial scale for HCl removal. These adsorbents had spherical shape with the particle diameter of 5-5.5 mm.

One of the samples was a simple ɣ-alumina, a typical adsorbent used as desiccant. This material was supplied by BDH Chemicals Ltd, having the mesh size 4-8.

The last adsorbent, further referred to as samples 1, was prepared by incipient wetness impregnation method using simple ɣ-alumina as a support.

Incipient wetness impregnation method, also known as dry impregnation or capillary impregnation is a commonly used technique for preparing supported materials and sample 1 have been prepared according to this technique which is described elsewhere [48,98].

Prior to impregnation, ɣ-alumina was sieved to 300-500 microns and dried for 2 h at 120°C. This was done to remove all the moisture from the material pores, so that the error in the determination of pore volume, which is the next step, is minimized.

After alumina was cooled to room temperature, its pore volume was determined by taking 4 g of dried material and adding distilled water under continuous stirring. When the incipient wetness point was reached, the volume of added water was read from the burette. The pore volume of ɣ-alumina was found to be 0.54 cm^3/g which is close to values found in the literature [21,53].

Aiming to prepare a sample of promoted alumina with a degree of sodium carbonate promotion of 8.2 wt% (equivalent to 5 wt% Na_2O on the surface[1]), ɣ-alumina (4 g) was dried at 120°C for 2 h and then impregnated to incipient wetness with 2.16 cm^3 of 2.17 M solution of $Na_2CO_3 \cdot 10H_2O$ (0.9646 g decahydrate/1.55 cm^3 solution) at 20°C under stirring conditions. The sample was then dried at 120°C for 18 h in order to remove the water, depositing the active phase on the alumina surface.

It is important to remark that the volume of solution added to the support should be equal to the pore volume of the alumina. When the volume of the solution is higher than the pore volume, solution transport changes from a capillary process to a diffusion one, the latter being much slower.

Because of this, 0.9646 g of decahydrate was dissolved in 1.55 cm^3 water instead of 2.16 cm^3 which corresponds to the pore volume of 4 g of adsorbent, since 0.9646 g decahydrate contains 0.6071 g H_2O (0.6082 cm^3 H_2O at 20°C). The volume of 10 mol of water at 20°C together with the volume of water in which the salt was dissolved gives the 2.16 cm^3 H_2O which is the total pore volume of 4 g of adsorbent.

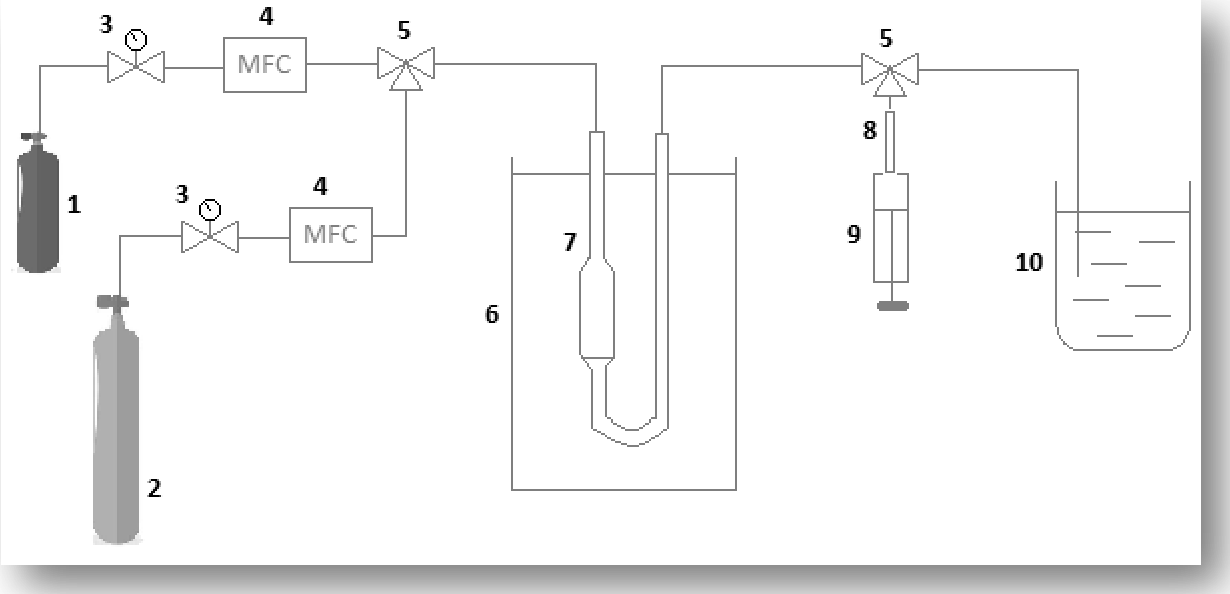
5.3 Experimental setup for HCl adsorption tests

HCl adsorption tests were carried out in a U glass tube made of borosilicate glass (fig.18) Adsorption tube (d=11 mm, L=70 mm) was filled with 4 g of adsorbent sieved to 300-500 microns, the length of the packed bed ranging from 51-58 mm depending on adsorbent material. Adsorption tube was placed in a water bath equipped with a heating immersion circulator MP, manufactured by Julabo Labortechnik GmbH, which maintained the temperature constant (40°C). Prior to each experiment, in order to remove the moisture present in the system and any traces of HCl, N_2 was flowed through the U glass tube at a constant flow rate of 2000 l/min. for 20 min.

Afterwards, the tube was filled with the adsorbent sample (4 g) and placed in the water bath for 30 min. Upon reaching the experimental temperature, a gaseous mixture of N_2 and HCl (4500 ppmv), contained in a 10 l gas bottle, was fed to the U-tube at a constant flow rate of 600 ml/min.

---

[1] From the stoichiometry of HCl reaction with Na_2O and Na_2CO_3, it can be found that the same amount of contaminant is removed by surface reaction on ɣ-Al_2O_3 impregnated with 5 wt% Na_2O and ɣ-Al_2O_3 impregnated with 8.2 wt% Na_2CO_3.



1 - gas cylinder (10 l) filled with N_2+HCl (4500 ppmv)
2 - gas cylinder (50 l) filled with pure N_2.
3 - pressure regulator
4 - mass flow controller
5 - 3-way valve
6 - temperature controlled water bath
7 - U glass tube with a filter
8 - HCl detector tube
9 - sampling pump
10 - absorber

Figure 18: *Schematic representation of the experimental setup*

The constant flow rates of the feed gas mixture (N_2+HCl) and of pure N_2 used for purging were maintained by using mass flow controllers, manufactured by MKS Instruments.

In the outlet of the adsorption tube, a Berzelius beaker filled with 2 l of an aqueous solution of NaOH 1M was placed. The purpose of the beaker filled with alkaline solution was to absorb any HCl flowing from the adsorption tube. To ensure that absorption takes place and the solution has a alkaline pH, a solution of 0.5% phenolphthalein was prepared and added to the beaker.

Analysis system consisted of HCl detector tubes manufactured by Gastec and a sampling pump (GV-100S) delivered by the same manufacturer. Three different types of tubes were used during the experiments: 14L, 14M and 14R. 14L tubes can detect HCl in gaseous streams in concentrations ranging from 0.2-76 ppmv, 14M detect somewhat higher concentration of HCl - 10-1000 ppmv, while 14R can easily identify HCl in concentrations ranging from 50-5000 ppmv.

Detector tubes are filled with a solid reagent that changes its color upon reacting with HCl. The concentration of HCl is then easily read at the interface of the stained-to-unstained reagent. Detector tubes are designed to measure the level of HCl within temperature range 0-40°C and relative humidity range 0-90%, with no correction for either temperature or humidity required.

Samples of effluent from the outlet of the U glass tube were taken once in 15 min., each time up to 5 pump strokes being required to read the HCl concentration. Each pump stroke required 30-45 seconds. For determining the breakthrough point more exactly (with an error of ±2 min.) all the experiments were repeated at least for 2 times, the frequency of taking samples increasing from 1 sample in 15 min. to 1 sample in 2 min.

Upon reaching the breakthrough point, some of the experiments were continued in order to plot the whole breakthrough curve (when needed), while in other cases, when being interested just in catching the breakthrough point and recording the initial slope of the breakthrough curve, experiments were stopped when the HCl concentration in the outlet of the adsorbent bed was higher than 100-200 ppmv.

When finishing the experiment, the U-tube was flushed with N_2 for 10 min. Afterwards the saturated adsorbent was discharged and the procedure for starting a new experiment was initiated all over again.

6 Results and discussion

6.1 Adsorption capacity

Adsorption capacity is one of the most important characteristics of an adsorbent material. It differs from one adsorbent to another, depending on such parameters as pore volume of the material, surface area, degree of promotion, etc. All these parameters are undoubtedly very important in the formulation of adsorbents. However, the purpose of these solid materials is to remove contaminants and that is why it is very important to know in the first place to what extent one adsorbent is able to do its job.

Performing experiments, adsorption capacities of the 2 commercial samples (A and B) were determined. Experiments with both adsorbent A and B were carried out at 40°C and in order to find their HCl removal capacity, breakthrough curves were obtained. These are presented in figures 19 and 20.

It could be seen in the figures above that the breakthrough curve of both adsorbents are S-shaped, being somewhat similar to the idealized breakthrough curve presented in figure 17.

When beginning the experiments, a mixture of 600 ml/min N_2+HCl started flowing through the adsorption tube filled with an adsorbent sample (4 g). As HCl was adsorbing from the feed mixture on the surface of the solid material, at the very beginning of the experiment no HCl was found in the outlet of the adsorbent bed. Adsorbent was capable of lowering the contaminant concentration from 4500 ppmv down to below 0.2 ppmv (the limit of detection), which is much lower than the imposed breakthrough concentration of 1 ppmv.

However, after a certain period of time, called breakthrough time, small amounts of HCl started escaping from the adsorbent bed. After 74 min (adsorbent A) and 144 min (adsorbent B), the concentration of HCl in the outlet of the adsorption tube was 1 ppmv.

Since the desired concentration of HCl in the refinery streams is below 1 ppmv, the adsorbent reaching the breakthrough point can be called "saturated" or "spent", as it cannot further satisfy the above-mentioned specification. The capacity of an adsorbent corresponding to the breakthrough point can be called effective capacity, since it is strongly dependent on the breakthrough concentration set by the operators. However, the real capacity of an adsorbent corresponds to the maximum amount of contaminant that can be adsorbed.

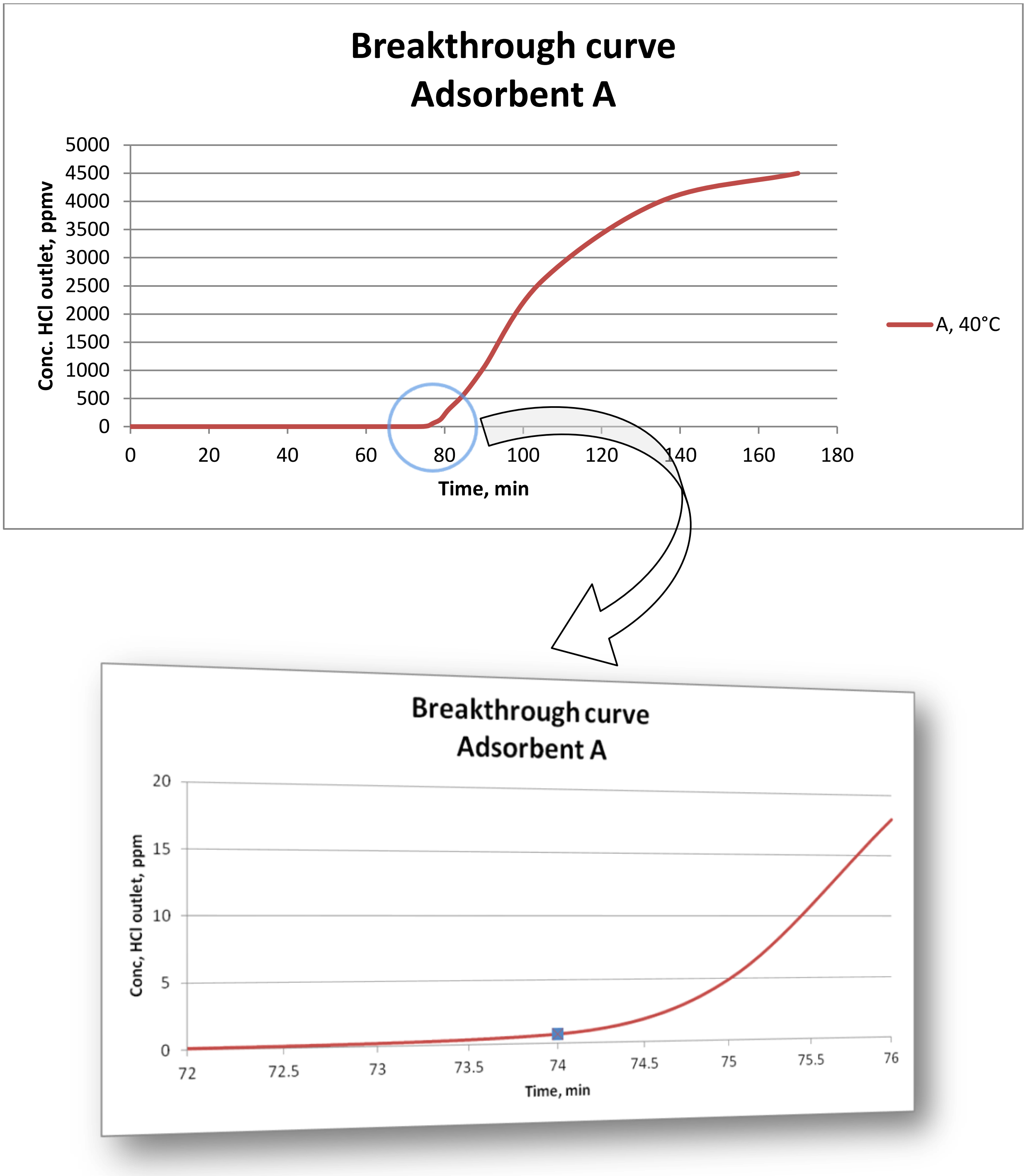


Figure 19: *Breakthrough curve of adsorbent A (T=40°C, Feed flow rate = 600 ml/min, 4g of adsorbent)*

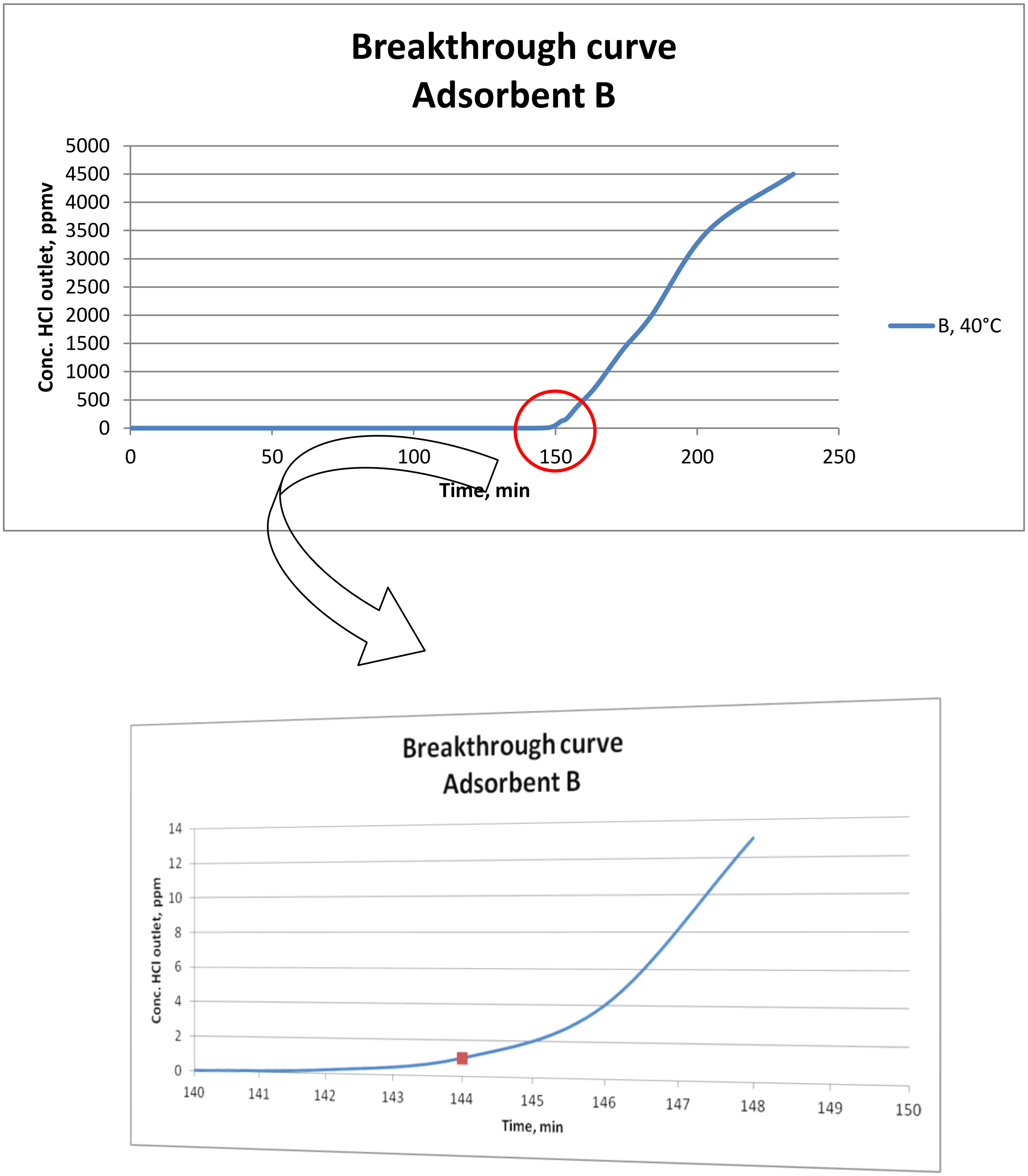


Figure 20: *Breakthrough curve of adsorbent B (T=40°C, Feed flow rate = 600 ml/min, 4g of adsorbent)*

When continuing the experiment, it could be seen that adsorption still took place, but to a lesser extent. The concentration of HCl in the outlet of the adsorption tube increased gradually to its concentration in the feed. In this way, after 170 min (adsorbent A) and 234 min (adsorbent B) no HCl was adsorbed anymore, solid material reaching its maximum adsorption capacity. When no more contaminant adsorbs on the solid surface, the adsorbent is called saturated.

In industry, operators does not wait until an adsorbent bed becomes saturated, the material being considered spent and is being discharged when the breakthrough capacity is reached.

In order to calculate the amount of HCl adsorbed on the surface of each adsorbent, a mass balance over the fixed bed should be done.

Mass balance over the fixed-bed of adsorbent:

(Accumulation of HCl) = (Input of HCl) - (Output of HCl)

(Input of HCl) :

$$\frac{dm_{HCl}^{in}}{dt} = Q \cdot C_{HCl}^{o} \cdot \rho_{HCl} \cdot 0.001 \tag{6.1}$$

(Output of HCl):

$$\frac{dm_{HCl}^{out}}{dt} = Q \cdot C_{HCl} \cdot \rho_{HCl} \cdot 0.001\,, \tag{6.2}$$

where

Q - feed flow rate (l/min)

C_{HCl}^{0} - concentration of HCl in the feed (ml HCl/m^3 mixture = ppmv)

C_{HCl} - concentration of HCl in the outlet of the adsorbent bed (ml HCl/m^3 mixture)

ρ_{HCl} - density of HCl at 40°C (g/l)

To find the accumulation of HCl and, thus, the capacity (*w*) of adsorbents A and B, equations 1 and 2 should be integrated over time.

$$w_A = 0.001 \cdot Q \cdot \rho_{HCl} \int_{0}^{t_{s,A}} (C_{HCl}^{0} - C_{HCl})dt \tag{6.3}$$

$$w_B = 0.001 \cdot Q \cdot \rho_{HCl} \int_{0}^{t_{s,B}} (C_{HCl}^{0} - C_{HCl}) dt \,, \tag{6.4}$$

where

$t_{s,A}$ *and* $t_{s,B}$ - the time is takes for adsorbents A and B to reach their saturation point.

The initial concentration of HCl is known, this being 4500 ppmv. However, the outlet concentration is not constant, varying from below 0.2 ppmv (considered 0 ppmv) to 4500 ppmv when adsorbent reaches its saturation level. Because of this, in order to calculate the capacity of adsorbents A and B, the effective capacity (w_1), corresponding to the amount of HCl adsorbed from time zero to the breakthrough time, and the capacity corresponding to the amount of HCl adsorbed from the breakthrough up to the saturation point (w_2), will be calculated separately.

The density of HCl at 40°C is:

$$\rho_{HCl} = \frac{PM}{RT} = 1.422\, g/l \tag{6.5}$$

Thus,

$$w_{1,A} = 0.001 \cdot Q \cdot \rho_{HCl} \int_{0}^{73} (C_{HCl}^{0} - C_{HCl}) dt = 0.2803\, g\, HCl \tag{6.6}$$

For calculating $w_{2,A}$, the breakthrough curve is approximated to a polynomial function of third order in the interval 73-170 min (fig. 21).

Thus,

$$C_{HCl} = -0.0047t^3 + 1.155t^2 - 13.527t - 3588.6 \tag{6.7}$$

and

$$w_{2,A} = 0.001 \cdot Q \cdot \rho_{HCl} \int_{73}^{170} (C_{HCl}^{0} - C_{HCl}) dt = 0.1282\, g\, HCl \tag{6.8}$$

The total amount of HCl adsorbed is therefore:

$$w_A = w_{1,A} + w_{2,A} = 0.4085\, g\, HCl \tag{6.9}$$

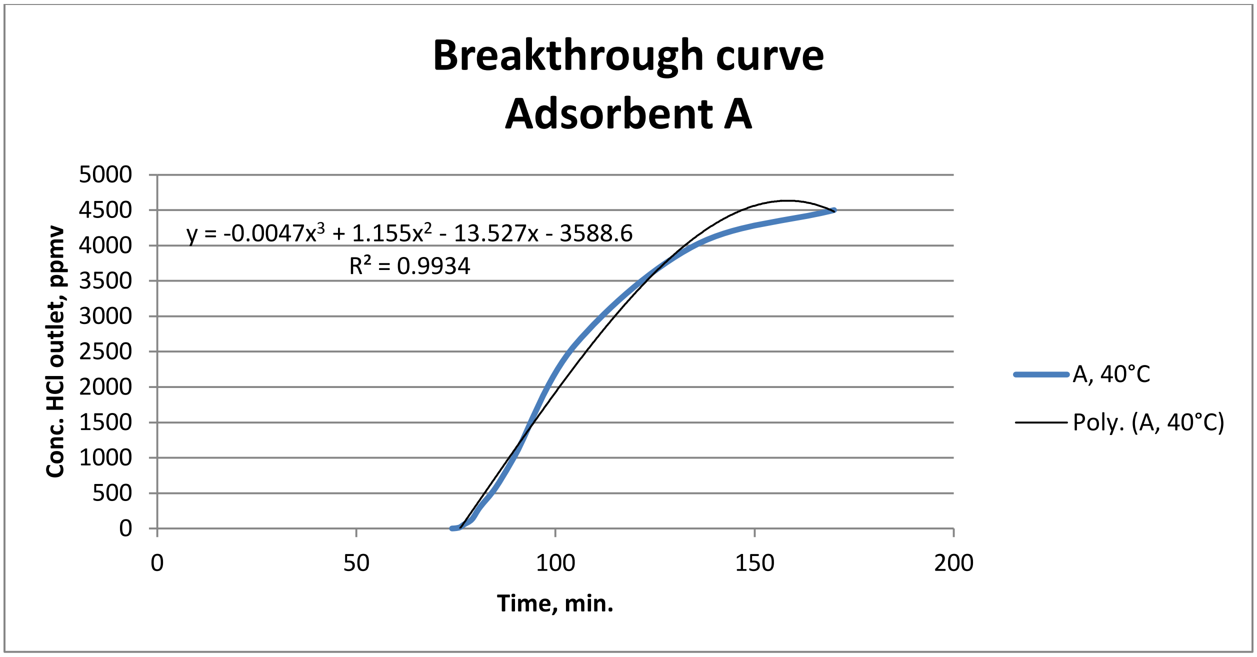


Figure 21: *Approximation of the breakthrough curve for adsorbent A in the interval 73-170 min.*

Since the adsorbent bed contained 4 g of adsorbent, the capacity of adsorbent A is:

$$W_A = \frac{w_A}{4} = 0.102\ g\ \ HCl/g\ adsorbent = 0.099\ g\ \ Cl^{-}/g\ adsorbent \qquad (6.10)$$

Same procedure is applied for finding the adsorption capacity of adsorbent B.

In this case, the breakthrough time is 144 min., $t_{s,B}$ is 234 min. and the breakthrough curve of adsorbent B is approximated to a polynomial function of third order in the interval 143-234 min (fig. 22).

The variation of HCl concentration in time after the breakthrough point is described by the following function:

$$C_{HCl} = -0.0122x^3 + 6.8323x^2 - 1197.8x + 67285 \qquad (6.11)$$

Therefore,

$$w_{1,B} = 0.001 \cdot Q \cdot \rho_{HCl} \int_{0}^{143} (C_{HCl}^{0} - C_{HCl})dt = 0.5490\ g\ HCl \qquad (6.12)$$

$$w_{2,B} = 0.001 \cdot Q \cdot \rho_{HCl} \int_{143}^{234} (C_{HCl}^{0} - C_{HCl})dt = 0.1547\ g\ HCl \qquad (6.13)$$

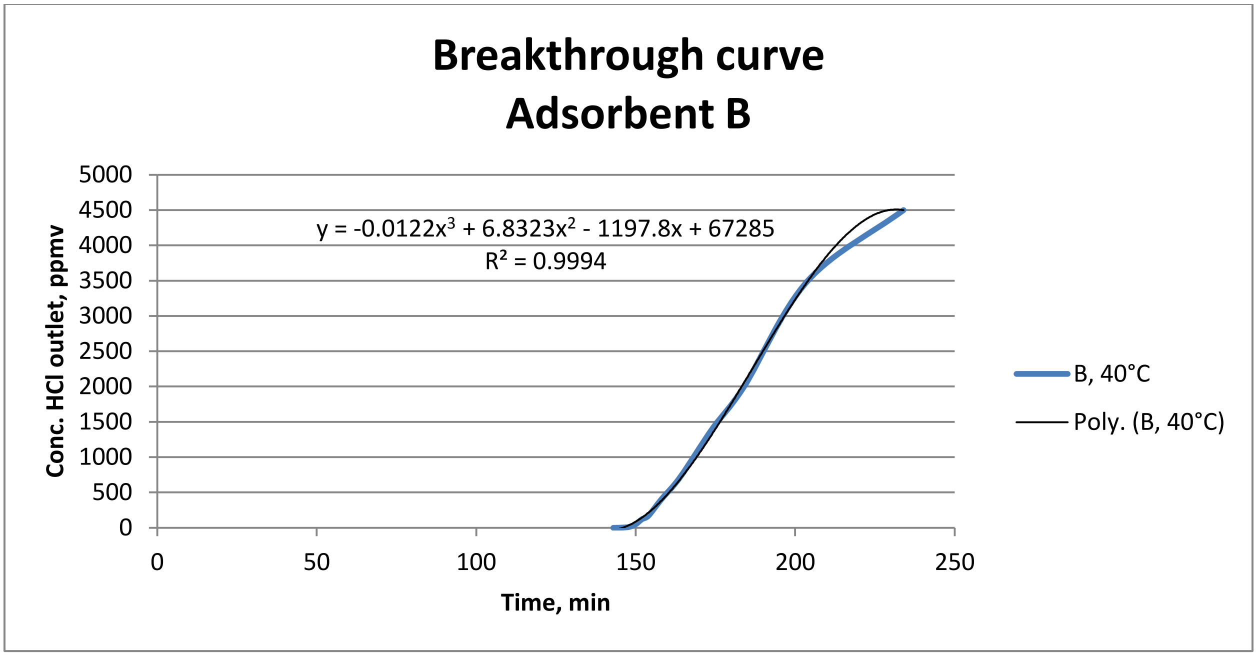


Figure 22: *Approximation of the breakthrough curve for adsorbent B in the interval 143-234 min*

The total amount of HCl "trapped" by adsorbent B is:

$$w_B = w_{1,B} + w_{2,B} = 0.7037\ g\ HCl \tag{6.14}$$

Considering that 4 g of adsorbent B were used for experiments, the HCl removal capacity of this material is:

$$W_B = \frac{w_B}{4} = 0.176\ g\ \ HCl/g\ adsorbent = 0.171\ g\ \ Cl^{-}/g\ adsorbent \tag{6.15}$$

In conclusion, the total adsorption capacity of adsorbent A at 40°C is 10.2 wt% HCl, the capacity of this material at breakthrough concentration 1 ppmv being 7 wt% HCl.

The removal capacity of adsorbent B at 40°C is somewhat higher, being 17.1 wt% HCl. The capacity of B at breakthrough concentration 1 ppmv is 13.7 wt% HCl.

The shapes of the breakthrough curves of adsorbents A and B appear quite different, this fact suggesting different kinetics of HCl adsorption. Moreover, the shape of the curve after the breakthrough corresponding to HCl adsorption on sample A suggests that there can be some mass transfer limitations. However, a detailed analysis of the adsorption kinetics is not performed since it lies outside the aim of this project.

The fact that adsorbent B has a higher removal capacity for HCl at breakthrough concentration 1 ppmv can be related to either its higher porosity, higher surface area or higher degree of promotion in comparison to adsorbent A. If higher porosity of adsorbent B is responsible for a later breakthrough of HCl then, most likely, physisorption is the dominant mechanism for the process, while if B contains a higher concentration of promoter on its surface or its surface area is greater (more Lewis and Brønsted acid sites) than that of adsorbent A then removal of HCl relies mostly on chemisorption.

In order to check this, adsorbents were tested at different temperatures.

6.2 Effect of temperature on adsorption process

Temperature is a parameters that can affect the adsorption process. As mentioned earlier in this work (see *Factors affecting adsorption*), temperature is influencing both kinetics and thermodynamics of adsorption. Neither close analysis of adsorption kinetics nor analysis of adsorption thermodynamics was the aim of this work, so that the variation of such parameters as: rate of adsorption or surface reaction rate, enthalpy of adsorption or reaction, free Gibbs energy of adsorption or reaction, were not evaluated.

However, by performing adsorption experiments at different temperatures and plotting the breakthrough curves for the tested adsorbents, some information regarding the mechanism(s) driving the process can be obtained.

In this sense, removal of HCl by adsorbents A and B was performed at 60°C and 80°C, the results being compared with the ones obtained from HCl adsorption on these materials at 40°C.

The breakthrough curves of adsorbents A and B at 40°C, 60°C and 80°C are presented in figures 23 and 24.

In the first place, it should be notice that the experiments at higher temperature were not run until the saturation of the adsorbents. The purpose was to catch the breakthrough point and compare the delay times (breakthrough times) before the concentration of HCl in the outlet of adsorbent tube reached 1 ppmv and started further to increase steadily.

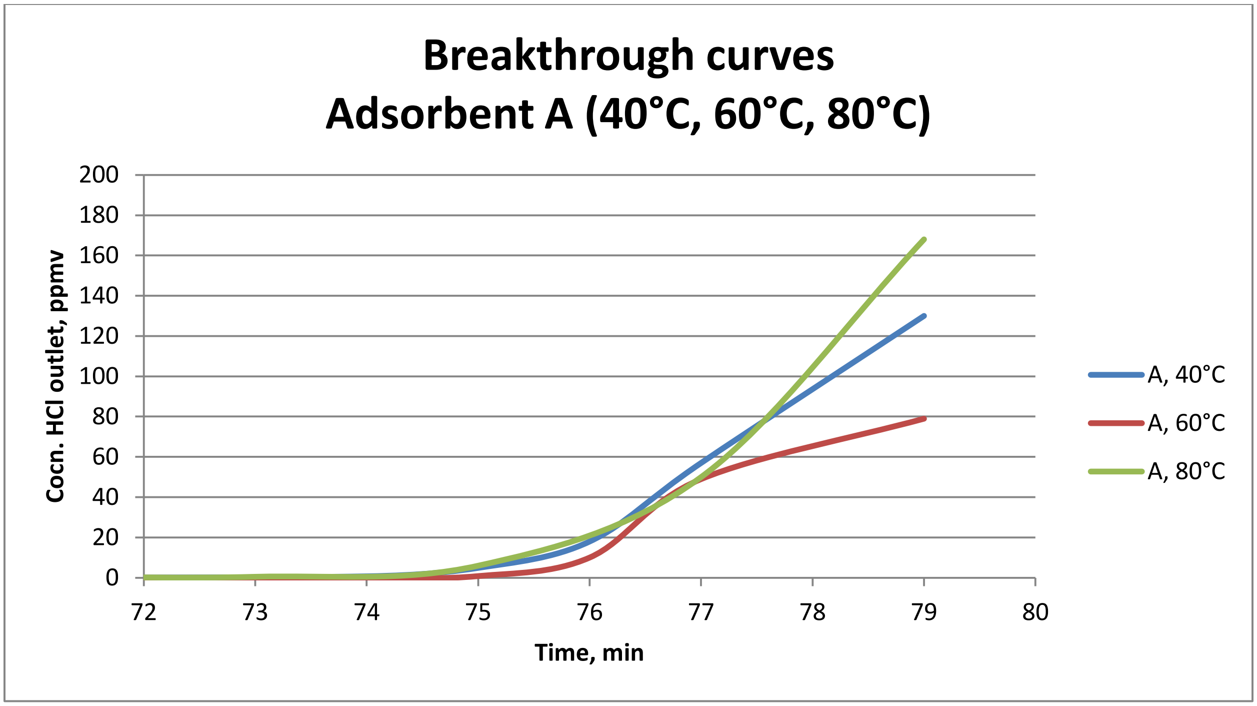


Figure 23: *The breakthrough curves of adsorbent A at 40°C, 60°C and 80°C (Feed flow rate = 600 ml/min, 4 g of adsorbent)*

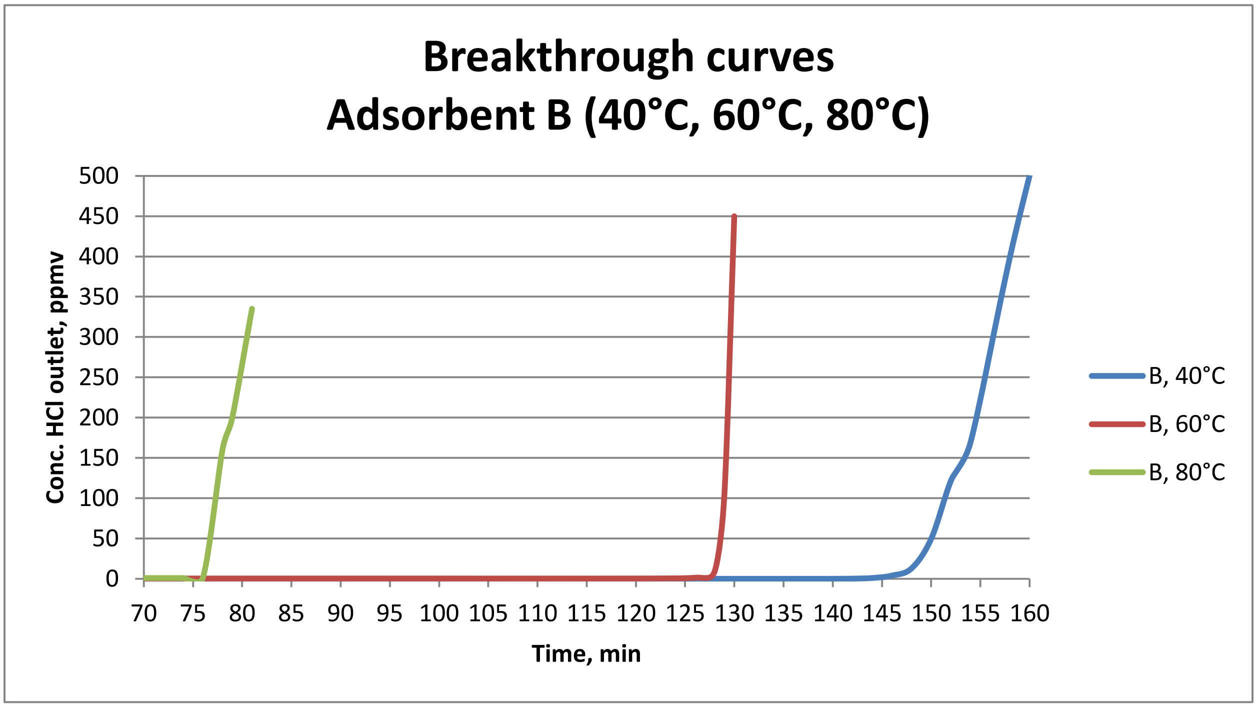


Figure 24: *The breakthrough curves of adsorbent B at 40°C, 60°C and 80°C (Feed flow rate = 600 ml/min, 4 g of adsorbent)*

From figure 23, it could be seen that the breakthrough times of adsorbent A at all the three temperature levels are in the same region (74-75 min.). Even if experiments were not run until the full saturation of adsorbent, this fact indicates clearly that the HCl removal capacity of adsorbent A is not dependent on temperature. Thus, it could be ascertained that almost all HCl from the feed was chemisorbed on the solid surface, physisorption taking place to a very little extent if at all.

Chemisorption of HCl on an alumina-based adsorbent can take place on both Lewis and Brønsted acid sites, but also due to the reaction of HCl with the promoter homogeneously distributed on the alumina support (see *Activated alumina and promoted alumina*). Since it is not known if adsorbent A is a promoted alumina or a simple alumina, the exact mechanism of chemisorption cannot be identified.

From the breakthrough curves of adsorbent B at 40°C, 60°C and 80°C it can be seen that the breakthrough times of this material and, intrinsically, its adsorption capacity for HCl varies quite a lot with temperature (table 3).

For instance, when rising the adsorption temperature with 20°C (from 40°C to 60°C), the effective capacity of adsorbent B reduced by 17.7%, whilst at 80°C it dropped down to only 47.4% of the effective capacity at 40°C. In this way, the effective capacity of B at 80°C almost equated that of A at 40°C.

Table 3: *Breakthrough times of adsorbent B at 40°C, 60°C and 80°C*

Temperature, °C	Breakthrough time, min
40	144
60	126
80	77

$$W_{B,40^\circ C}^{effective} = \frac{0.001}{4} \cdot Q \cdot \rho_{HCl}^{40^\circ C} \int_0^{144} (C_{HCl}^0 - C_{HCl})dt = 0.1382\ g\ \ HCl/g\ adsorbent \quad (6.16)$$

$$W_{B,60^\circ C}^{effective} = \frac{0.001}{4} \cdot Q \cdot \rho_{HCl}^{60^\circ C} \int_0^{126} (C_{HCl}^0 - C_{HCl})dt = 0.1137\ g\ \ HCl/g\ adsorbent \quad (6.17)$$

$$W_{B,80^\circ C}^{effective} = \frac{0.001}{4} \cdot Q \cdot \rho_{HCl}^{80^\circ C} \int_0^{77} (C_{HCl}^0 - C_{HCl})dt = 0.0655\ g\ \ HCl/g\ adsorbent, \quad (6.18)$$

where the densities of HCl are: 1.422 g/l (40°C), 1.337 g/l (60°C) and 1.261 g/l (80°C), being calculated using the ideal gas equation(eq. 6.5).

If previously it was though that the higher effective HCl removal capacity of adsorbent B in comparison with the effective capacity of adsorbent A is related to either the higher degree of promotion of the former, its higher porosity or higher surface area, it is quite clear now that either the degree of promotion of adsorbent B is at most equal[2] to the degree of promotion of its "confrere" A (in case A is a promoted alumina) or B has a surface area not higher than that of A (in case A is not a promoted alumina). Therefore, the porosity is probably playing an important role in HCl removal on B surface. The share of chemisorption in the overall adsorption mechanism is not even close to 100%, representing at most 47.4%. In order to make an even better approximation, experiments at higher temperatures should have been carried out.

To support the above made theory, though, experiments with a simple ɣ-alumina were carried out at 40°C and 60°C (fig. 25).

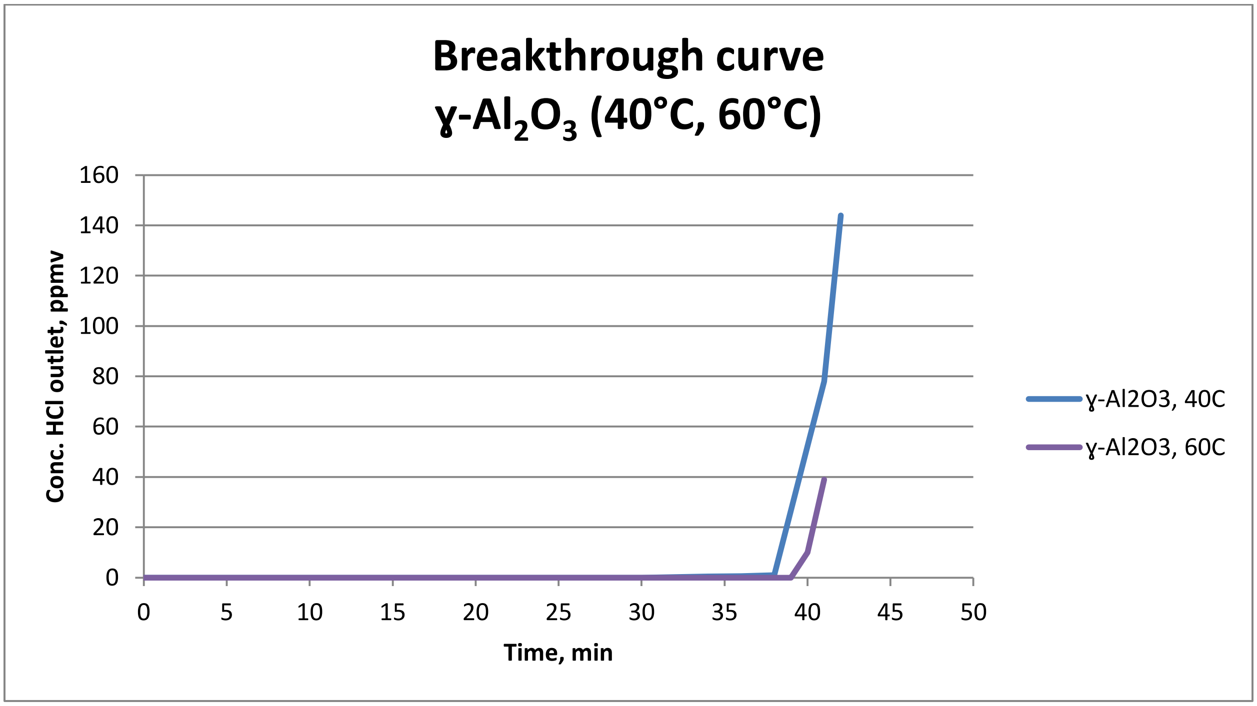


Figure 25: *Breakthrough curves of simple ɣ-Al_2O_3 at 40°C and 60°C (Feed flow rate = 600 ml/min, 4 g of adsorbent)*

First thing that could be observed in figure 25 is that the effective HCl capacity of simple ɣ-alumina is similar at 40°C and 60°C. This can only mean that HCl is almost totally removed by chemisorption. This is in agreement with what was found in the literature (see *Activated alumina and promoted alumina*), the fact that physisorption is suppressed being probably

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[2] Here "equal" referring to an equivalent amount of promoter. For instance, a sample containing 8.2 wt% Na_2CO_3 will remove by chemisorption the same amount of HCl as a sample containing 5 wt% Na_2O (results from stoichiometry of the reaction of promoter with HCl).

caused by the low porosity of this sample. The pore volume of ɣ-alumina was found to be 0.54 cm^3/g which is an average value for these materials [99]. Furthermore, its effective HCl capacity is almost half of that of sample A and sample B at 80°C.

The fact that removal of HCl by both A and ɣ-alumina relies mostly on chemisorption and that the effective capacity of A is higher suggests that the total pore volume of both materials is quite similar, A having either a higher surface area or, more likely being promoted.

Taking into consideration that both A and B are alumina-based adsorbents and that the effective capacity of B at 80°C equates that of A at 40°C, it can be suggested that B might be even less promoted than A. As stated earlier, experiments with B at higher temperature should be run. Nevertheless, in case this statement is true, it can be suggested that adsorption of HCl on B relies mostly on physisorption due to the most probably highly porous alumina used in the formulation of this material.

It is worth mentioning that when sieving adsorbent to 300-500 microns it has been noticed that the crushing strength of adsorbent B is lower than that of both adsorbent A and simple ɣ-alumina. Moreover, when loading the U-tube with an adsorbent sample (4 g) it has been observed that the height of the fixed bed was greater for adsorbent B than for A and ɣ-alumina (table 4). These facts together suggest that indeed the total pore volume of adsorbent B is higher than that of A and simple ɣ-alumina, the share of physisorption being probably higher than 52.6% as thought before.

Table 4: *Height of adsorbent bed for different adsorbents*

Adsorbent	Bed height, cm
A	5.1
ɣ-alumina	5.2
B	5.8

Considering the results registered from the experiments with A, B and ɣ-alumina at different temperature levels, it can be concluded, with a quite high probability, that:

- Adsorbent A is promoted to some extent, since no signs of physisorption can be found by analyzing its breakthrough curves and its effective HCl removal capacity is greater than that of ɣ-alumina, which was also found to be a chemical adsorbent.

- Adsorption of HCl on B relies to a great extent on physisorption, its share being probably higher than 52.6%, but at least as high as this value. To find this out, as mentioned earlier, experiments with B at higher temperature should be run.

It should be mentioned also that when running experiments with both A and B at 80°C, the outlet concentration of HCl was not less than 0.2 ppmv as when testing these adsorbents at 40° or 60°C. Instead, it was oscillating between 0.3-0.7 ppmv until the breakthrough of HCl occurred. This is quite peculiar and can be explained only by the fact that detector tubes are designed to provide with reliable results in the temperature range 0-40°C. However, at 60°C the strange oscillation in the outlet HCl concentration before the breakthrough was not registered. More experiments should be run at temperatures higher than 40°C in order to understand this behavior and a method to cool the U-tube effluent before taking a sample should be applied.

6.3 Effect of mass transfer limitations on adsorption of HCl

Adsorption process can be affected by mass transfer resistances. In order to adsorb on a solid surface, solute have to diffuse through a thin film around the particle to the external surface of the adsorbent, and then, since the internal surface area of adsorbents is much higher than the external one, into the pore structure of the solid material (see *Background*).

In order to ensure a low or no external mass transfer resistances, the flow rate of the fluid(solute) and the concentration of the solute in that fluid phase should be high enough [100]. In turn, for eliminating internal mass transfer limitations, adsorbent particles should be reduced in size, thus making the pathway of the solute to the internal surface area of the solid material shorter [53].

For quantifying the effect of the external and internal mass transfer resistances, a detailed kinetic analysis should be performed. Upon such an analysis, parameters as Thiele modulus, internal effectiveness factor, external effectiveness factor or the overall effectiveness factor, are calculated.

Thiele modulus represents, in this case, the ratio of the surface adsorption rate to the internal diffusion rate. Internal effectiveness factor gives the ratio of the actual overall adsorption rate to rate of adsorption in presence of internal mass resistance. The overall effectiveness factor representing the ratio of the actual overall adsorption rate to the rate of adsorption that would results if the entire surface of an adsorbent particle were exposed to bulk conditions [101].

However, determination of these parameters lies outside the aim of this work.

__External mass transfer limitations__

In order to recognize if the adsorption process is affected by external mass transfer limitations, experiments on HCl adsorption on adsorbent A were carried out at 2 different linear gas velocities. In the first place, contaminant removal from the gaseous feed was done by flowing the latter through a bed packed with 2 g of adsorbent A at a flow rate of 300 ml/min. The resulted breakthrough curve was compared with the one obtained upon adsorption of HCl on 4 g of A at a feed flow rate of 600 ml/min. Both breakthrough curves are sketched in figure 26. Only the breakthrough points were of interest, so that experiments were stopped shortly after the breakthrough of HCl occurred.

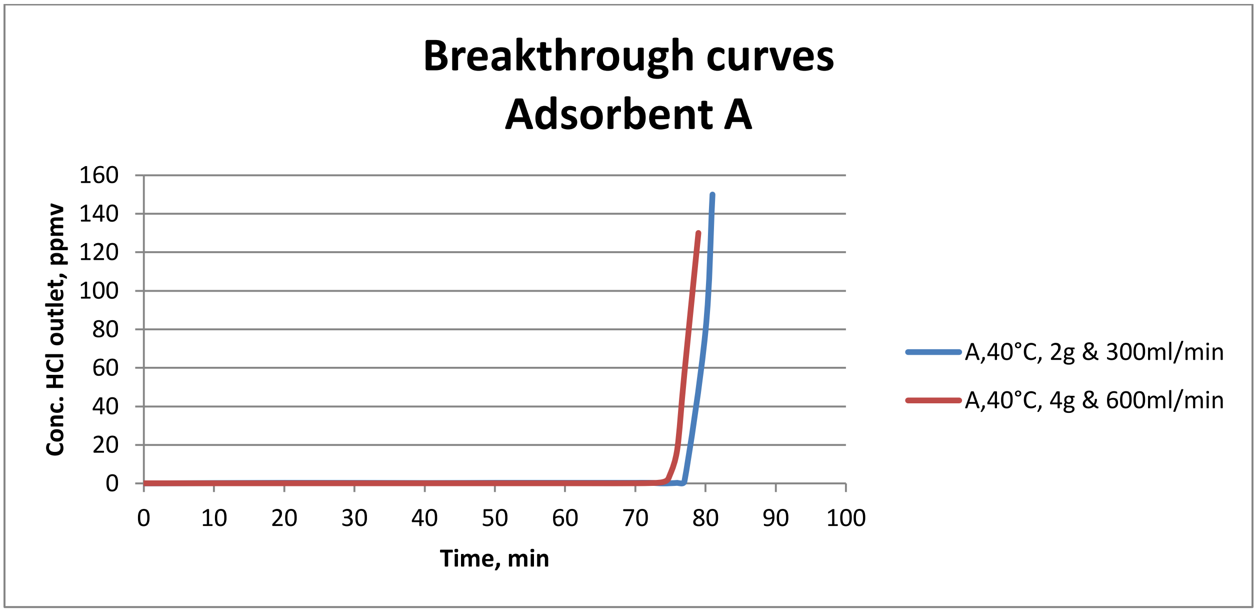

Figure 26: *The breakthrough curves of adsorbent A. Red: 4 g adsorbent, feed flow rate =600 ml/min.; blue: 2 g adsorbent, feed flow rate =300 ml/min.*

An increase in the amount of adsorbent by a factor of 2 implies an increase of the height-to-diameter ratio of the adsorbent bed by a factor of 2 which, in turn, translates into a rise of linear gas velocity by 100%. An increase in the linear velocity of the gas phase(solute) reduces the potential external mass transfer limitation. Moreover, an increase in the flow rate of the feed has the same effect on the external mass transfer resistance. This being said, it can be concluded that if adsorption of HCl on A is diffusion-limited(here referring to external diffusion) then the rate of adsorption in the first experiment (2 g adsorbent, 300 ml/min. feed flow rate) should be lower than in the second test. However this is not the case.

As mentioned earlier, a kinetic analysis was not performed. Nevertheless, by plotting the breakthrough curves and comparing the breakthrough times in the two cases, it can be seen that HCl breaks through the adsorbent bed approximately after the same period of time (≈ 74-77 min.) and the slope of the curves after the breakthrough are quite similar. This might suggest the fact that external diffusion of the HCl to the external surface of A does not perturb the overall adsorption process.

To support this suggestion, HCl adsorption was carried out on 4 g of A at a flow rate of 800 ml/min. The breakthrough curve obtained from these experiment is plotted together with the previous two in figure 27.

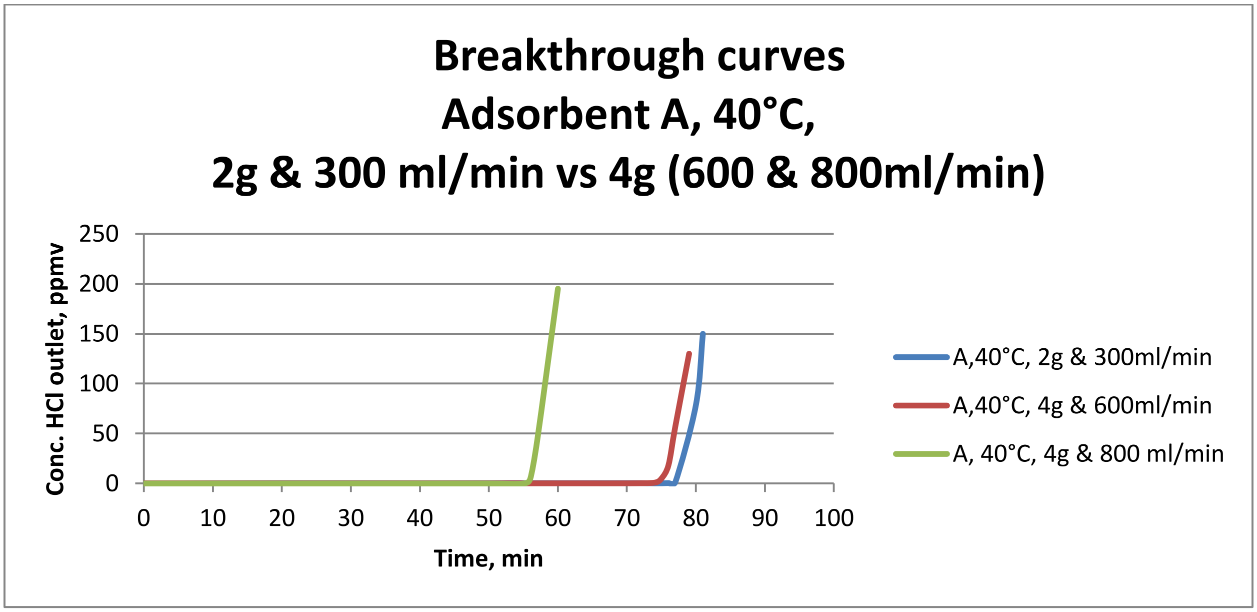

Figure 27: *Comparison between the breakthrough curves of adsorbent A at 40°C. Blue: 2 g adsorbent, feed flow rate = 300 ml/min; Red: 4 g adsorbent, feed flow rate 600 ml/min; Green: 4 g adsorbent, feed flow rate 800 ml/min.*

From figure 27 it can be seen that indeed the slopes of all the three curves are similar after the breakthrough. This strengthens the idea of the absence of external mass transfer resistance.

However, to prove this, the external effectiveness factor should be calculated. Also, in order to identify the region, in terms of flow rate and linear gas velocity variations, in which adsorption is not affected by external mass transfer limitations, experiments at sufficiently large flow rates of feed mixture and with a sufficiently large height-to-diameter ratios should be carried out. Unfortunately, this is not possible at lab scale. The linear gas velocity in an industrial scale adsorption vessel cannot be reproduced in a lab, this being one of the greatest challenges when scaling up the adsorption process.

In figure 27 it can also be noticed that HCl breakthrough occurred earlier in the last experiment of this series (green line). This is simply explained by the fact that the effective HCl removal capacity does not change when increasing the flow rate of the feed. If $W_{A,\,40°C}$ is the effective capacity of A at 40°C:

$$W_{A,40°C}^{effective} = \frac{0.001}{m} \cdot Q \cdot \rho_{HCl}^{40°C} \int_{0}^{t_b} (C_{HCl}^{0} - C_{HCl})dt\,, \tag{6.19}$$

where

m - mass of adsorbent (g)

t_b - breakthrough time (min.),

then

$$W_{A,4g\&800ml/min}^{effective} = \frac{0.001}{4} \cdot Q \cdot \rho_{HCl}^{40°C} \int_{0}^{55} (C_{HCl}^{0} - C_{HCl})dt = 0.7039\ g\ \ HCl/g\ adsorbent\,, \tag{6.20}$$

which is similar to the one that can be obtained from equation 6.6.

<u>Internal mass transfer limitations</u>

For identifying possible internal mass transfer limitations, adsorbent's particle size was used as a parameter. In this sense, two experiments were run, adsorbent A being sieved into two different size fractions: 300-500 microns and 50-300 microns. As in the previous experiments, the breakthrough curves were not recorded until the full saturation of the solid material. Experiments were stop shortly after the breakthrough point was reached, the results being sketched in figure 28.

As mentioned earlier, when the particle size decreases the diffusion rate of the solute from the external surface area of the solid material into its pores increases. This is explained by the fact that the pathway that the solute should "travel" from the external surface area into the pore structure of the adsorbent is shortened.

By looking at the breakthrough curves obtained from the two experiments, it could be concluded that the effective capacity of adsorbent A decrease when being sieved into smaller particles (50-300 microns). This can be explained by the fact that when crushing the adsorbent its integrity was destroyed. Since it is not known if adsorbent A is a promoted alumina or not, it can be that crushing resulted in either an inhomogeneity of promoter distribution (if A is promoted) or in pore occlusion.

The fact that the breakthrough time of the sample sieved to 50-300 microns is not larger than that of sample sieved to 300-500 microns and that the slopes of both breakthrough curves after the breakthrough point are quite similar, suggests that HCl adsorption on A is not affected by internal diffusion resistance.

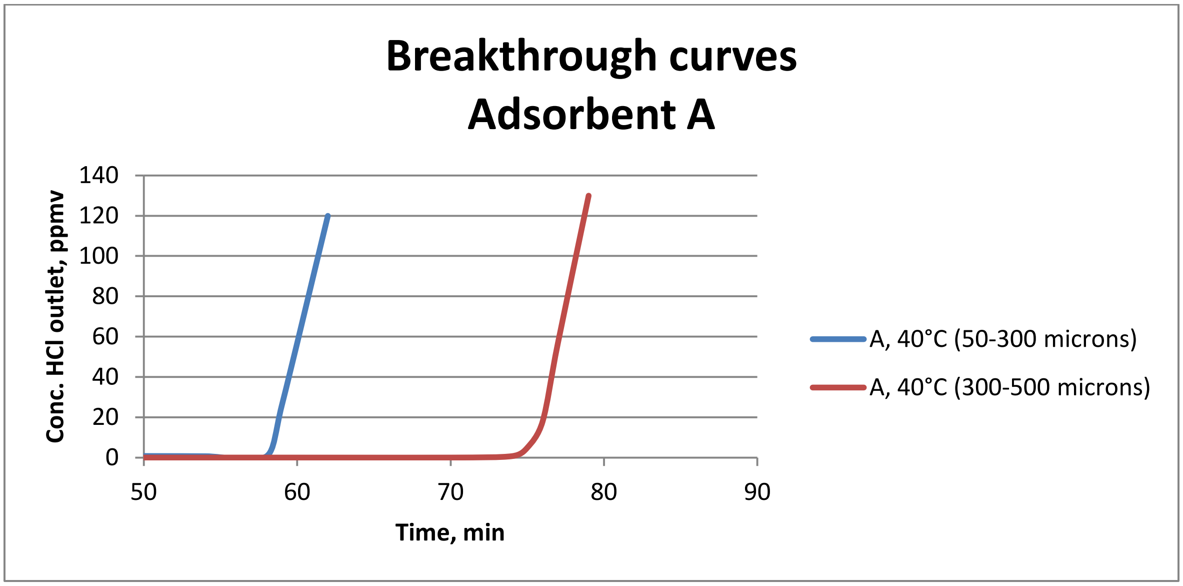

Figure 28: *The breakthrough curves of adsorbent A. Red: particles size 300-500 microns; blue: particles size 50-300 microns (T=40°C, Feed flow rate = 600 ml/min, 4g of adsorbent)*

In order to support this suggestion, though, Thiele modulus should be computed, this representing the ratio of the surface adsorption rate to the internal diffusion rate.

6.4 Effect of adsorbent promotion on adsorption process

One way of enhancing the adsorption capacity of an adsorbent is to deposit on its surface an active material. The purpose of this material, deposited usually on a high surface area support, is to react with the solute that diffuses from the bulk fluid phase to the internal and external surface of the adsorbent. In this way, the contaminant from the feed is removed not just by physisorption and/or chemisorption, but also by chemically reacting with the promoter, the synergism of these two or three removal mechanisms being responsible for a potential higher removal capacity of the promoted materials.

Promotion can play also a negative role. Generally, when depositing the promoter onto the surface of the support, the surface area of the latter decreases and therefore the amount of adsorbate that physisorbs onto the adsorbent surface decreases. Sometimes, promotion can even affect the porosity of the material, this happening when deposition of the promoter causes pore blocking [54]. Nevertheless, when an adsorbent is promoted with a reasonable quantity of promoter, the overall capacity given by all the mechanisms involved in the adsorption process increases.

However, when the degree of promotion is too high (excess of promoter on the surface of the support), both surface area and total pore volume decreases significantly and can reach the level which translates into an adsorption capacity of the material even lower than the one before deposition of the promoter.

To quantify to what extent the capacity of an adsorbent can be increased by promoting it, experiments with a ɣ-alumina sample promoted with 8.2 wt% Na_2CO_3 were carried out. The sample was prepared by incipient wetness impregnation method (see *Materials and samples preparation*). Experiments were run at 40°C at a feed flow rate of 600 ml/min.

The breakthrough curves of the simple ɣ-alumina and the prepared promoted alumina are plotted in figure 29.

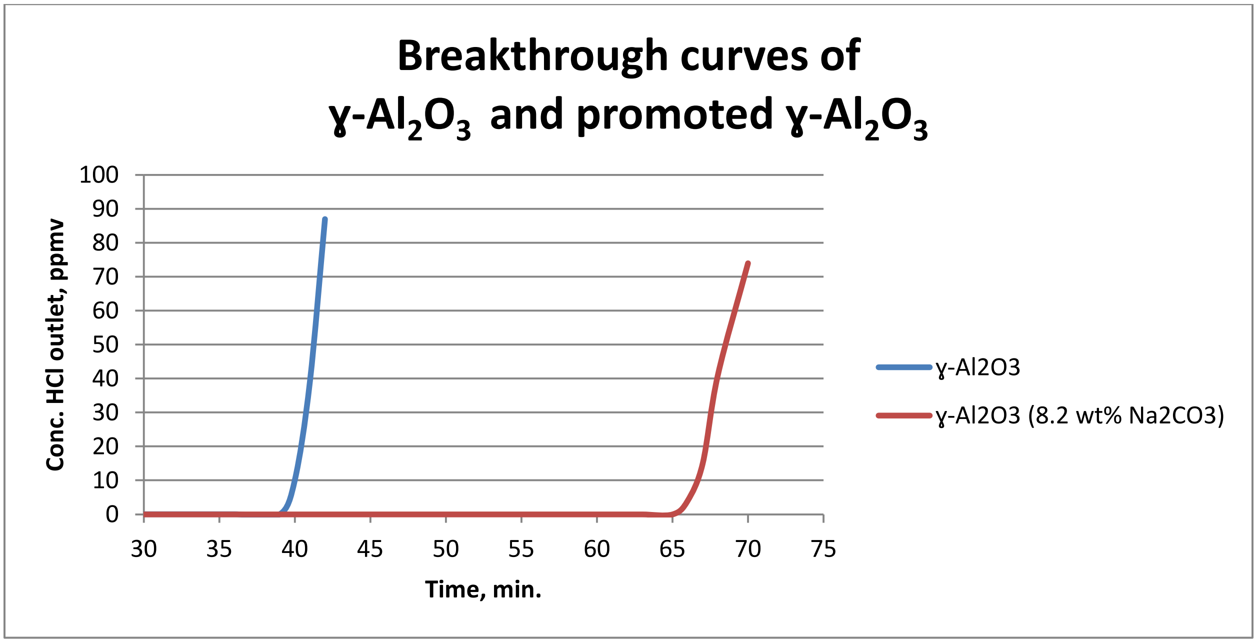

Figure 29: *Breakthrough curves of ɣ-Al_2O_3 and ɣ-Al_2O_3 promoted with 8.2 wt% Na_2CO_3 (T=40°, 4g of adsorbent,feed flow rate = 600 ml/min)*

From the plot (fig.29) it can be seen that indeed the promotion of alumina with Na_2CO_3 enhances its removal capacity for HCl.

The breakthrough time of the promoted sample (66 min.) increased by near 69%. The effective HCl removal capacity of both samples was calculated with equations 6.3 and 6.10. Thus, the effective capacity of ɣ-alumina, which has a breakthrough time of 39 min., is 0.0374 g HCl/g adsorbent, whilst the effective capacity of the promoted sample is 0.0633 g HCl/g adsorbent, which is higher by exactly 69%.

It is worth mentioning that by promoting ɣ-alumina with 8.2 wt% Na_2CO_3, the effective capacity of the product approached the effective HCl capacity of commercial adsorbent A (0.07 g HCl/g adsorbent). It could not be concluded earlier if A is a promoted alumina or just has a higher surface area than ɣ-alumina, but it could be said that if commercial adsorbent A is promoted, then its degree of promotion is very close to its equivalent of 8.2 wt% Na_2CO_3.

7 Suggestions for further work

In this work, adsorption of HCl on several alumina-based adsorbents was studied, the main goal being the development of a methodology for adsorbents' testing. For developing a system of methods that will help understanding the mechanisms behind HCl adsorption on different solid materials, evaluating the removal capacity and the efficiency of these adsorbents, but also explaining and, sometimes, quantifying the influence of various factors that affect the overall adsorption process, the breakthrough curves were used.

As mentioned in *Results and discussion* chapter, breakthrough curves of the adsorbents can offer information on a wide range of parameters that interfere with the adsorption of HCl on alumina-based materials. However, breakthrough curves alone cannot provide answers to all the questions.

For instance, by comparing the breakthrough curve of ɣ-alumina with those of commercial adsorbents A and B, it could be concluded that adsorption of HCl on ɣ-alumina and A relies mostly on chemisorption, whilst on adsorbent B physisorption of HCl is quite pronounced. Nevertheless, it was not possible to conclude exactly what makes the capacity of adsorbent A greater than that of ɣ-alumina or what makes adsorbent B have a capacity which is almost twice as high as that of A at 40°C. Quantification of the effect of such parameters as surface area, porosity, degree of promotion and others is not possible by using just the breakthrough curves, especially when the composition of the material is not known.

Therefore, in order to improve the methodology, one should test adsorbents with known compositions. Furthermore, experimental techniques that allow the measurement of surface area, total pore volume can be of great use and should be a part of the adsorbents' testing methodology.

Another good point in the future investigation of HCl adsorption on solid materials is to vary the parameters affecting the process within a wider range. In this work, for instance, experiments only with feed rates in the range 300-800 ml/min. were run and the results suggested that there no external mass transfer resistances that affect the adsorption process. Also, only two different adsorbent particle sizes were tried. However, at lower feed flow rates or when sieving the adsorbent into particles greater than 500 microns mass transfer limitations can appear and perturb the overall adsorption process. Therefore, it can be a good idea to delimit the region within which adsorption is not limited by either external or internal diffusion of the solute, this being done by performing tests over a wider range of parameters' variation.

Also, in the present work, only experiments with very high concentration of HCl in the feed (4500 ppmv) were carried out. This was done to adjust the time needed for adsorbents to reach the breakthrough point or, in some cases, saturation time, the latter, at industrial scale, being as large as 3-4 years. In reality, the concentration of HCl in such contaminated refinery streams as H_2, C_1-C_2 fraction, LPG and naphtha is less than 100 ppmv, being usually in the range 4-40 ppmv. Therefore, it could be useful to monitor the efficiency of the HCl adsorption on solid materials when the process is operated closer to real conditions.

It has been mentioned that adsorption of HCl on solid surfaces, usually physisorption, makes the surface highly acidic. Because of the fact that organochlorides are also most likely present in the system, these have tendency to polymerize, the polymerization reaction being favored by the acidic adsorbent surface. This raises the idea of performing an analysis on the influence of this phenomenon on the HCl adsorption on solid materials and, eventually, finding a way to adsorb organochlorides efficiently in parallel with HCl.

Additionally, experiments in which adsorbent bed is exposed to a real feed mixture containing hydrocarbons should be carried out. In this way it could be determined if a competitive adsorption of hydrocarbons takes place on solid materials and if so then to what extent.

Regeneration experiments were not run in this study. Nevertheless, the ability of a solid material to be regenerable upon saturation with HCl is an important aspect of an adsorbent, especially when being used at industrial scale. Therefore, regeneration tests with alumina-based adsorbents saturated with HCl should be carried out, firstly, for determining if adsorbent can be regenerated and, secondly, for finding the most efficient way of performing regeneration of the solid material so that its adsorption performance is not affected.

A last but not least suggestion for further work would be to make the sampling method handier. In this work a sampling pump and test tubes were used. To draw one gas sample using the sampling pump and a test tube, 30-45 seconds are required. Then the concentration of HCl should be read, test tube - changed and procedure repeated again. To determine precisely the variation of HCl concentration in the outlet of the adsorbent bed in time, samples should be taken quite frequently, the frequency increasing very much after the breakthrough point. Therefore, the person in charge is kept quite busy, the procedure being at the same time not very handy. Because of this, other methods for sampling should be evaluated.

It is important that a device is monitoring the concentration of HCl in real time and that its detection limit is below 1 ppmv. As a suggestion, FTIR spectrometer can be used in this sense. It has been reported [102] that FTIR spectroscopy is a powerful tool for HCl analysis, allowing detection of this contaminant from gaseous streams at levels below 1 ppm.

"It is always wise to look ahead, but difficult to look further than you can see"

Winston Churchill

8 Conclusion

The aim of this master thesis was to design a methodology for testing adsorbents used for HCl removal from refinery streams. For this purpose, alumina-based adsorbents were tested in adsorption of HCl from a gaseous feed under various conditions. The method used for adsorbents' testing totally relied on the analysis of the breakthrough curves which were obtained from each set of experiments.

This analysis made it possible to identify in the first place the mechanisms which drove the adsorption process. This was done by studying the influence of temperature on adsorption. By running experiments with adsorbent A and B under similar conditions (40,60,80°C, 4 g of adsorbent and 600 ml/min. feed flow rate), it was concluded that the adsorption of HCl on A relies almost totally on chemisorption, whilst adsorption on B is a physicochemical process, the share of physisorption in the overall adsorption mechanism being at least 52.6%. Moreover, by comparing the breakthrough curves of these two adsorbents with the breakthrough curve of simple ɣ-alumina, it could be suggested that adsorbents A and B have both either a greater surface area and, intrinsically, a higher concentration of Lewis and Brønsted acid sites on the surface, than ɣ-alumina or the former are promoted adsorbents.

Plotting of the breakthrough curves of adsorbents A and B made it also possible to calculate the HCl removal capacities of these solid materials. In this way, both the effective capacity (breakthrough capacity) and the designed capacity were calculated. The breakthrough capacities of A and B were found to be 7 wt% HCl/g adsorbent and 13.7 wt% HCl/g adsorbent accordingly, values which are within the 6-14 wt% range found in the literature [9]. The designed capacities, as expected, were found to be somewhat higher.

Besides studying the effect of temperature on the adsorption process, the effect of adsorbent promotion was quantified. A sample of alumina promoted with 8.2 wt% Na_2CO_3 (the equivalent of 5 wt% Na_2O) was prepared and its breakthrough capacity was compared with that of its precursor - ɣ-alumina. It was concluded that promotion with carbonate (8.2 wt%) has enhanced the HCl removal capacity of ɣ-alumina by 69%. Since, the breakthrough capacity of the prepared adsorbent was close but still lower than that of the commercial sample A, it could be concluded that if A is a promoted alumina then its degree of its promotion is quite close to the equivalent of 5 wt% Na_2O. It was, however, impossible to approximate the degree of promotion of the commercial adsorbent B since the share of physisorption in the overall adsorption mechanism of HCl removal on this material was not quantified.

Last but not least, an attempt to identify any mass transfer resistances that can affect the overall adsorption process was carried out. By comparing the breakthrough curves of adsorbent

A, in terms of breakthrough points and slopes, obtained from a series of tests run under different conditions (different flow rates, different adsorbent particle sizes), it could be suggested that adsorption was not affected by any mass transfer limitations. Nevertheless, this methodology appeared to be not quite accurate in evaluating the influence of mass transfer resistances on the HCl adsorption on solid materials. As it was suggested in the previous chapter, the proposed methodology for adsorbents' testing should be improved, in this sense, by complementing it with a kinetic analysis.

In conclusion it could be said that the methodology presented in this master thesis has space for improvement. Some suggestions on this have been made earlier in the report, but there are definitely more ways of refining the presented method for HCl removal adsorbents' testing.

9 References

[1] *Process analytics in vinyl chloride (VCM) plants*, Siemens AG, 2007. Available from: https://w3.siemens.com/mcms/sensor-systems/CaseStudies/Process_Analytics_in_VCM_Plants.pdf

[2] George Odian, *Principles of polymerization.* 4th Edition, Wiley & Sons, 2004 (p. 748-749).

[3] *Stimulate the flow*, Middle East & Asia Reservoir Review, No. 4, Schlumberger, 2003. Available from: http://www.slb.com/~/media/Files/resources/mearr/num4/stimulate_flow.pdf

[4] J.A. Moulijn, M. Makkee, A.E. Diepen, *Chemical Process Technology*, 2nd Edition, Wiley, 2003 (p. 65-67).

[5] V.A. Mazzieri, J.M. Grau, C.R. Vera, J.C. Yori, J.M. Parera, C.L. Pieck, *Role of Sn in Pt-Re-Sn/*Al_2O_3*-Cl catalysts for naphtha reforming*, Catal. Today **107-108** (2005) 643-650

[6] P.V. Broadhurst, *Removal of chloride compounds*, PTQ Q2, 2003. Available from: http://www.digitalrefining.com/article/1000301,Removal_of_chloride_compounds.html#.VX2zHM-eDRY

[7] *Hydrochloric acid (Hydrogen chloride),* Environmental Protection Agency, 2013. Available from: http://www.epa.gov/ttnatw01/hlthef/hydrochl.html

[8] J.G. Speight, *Fouling in refineries*, Elsevier Inc., 2015 (p. 167-170).

[9] P.R. Petersen, A. de Jong, W.F. Minyard, J.L. Sigmon, *Impact of ammonium chloride salt deposition on refinery operations*, Corrosion 2001, NACE International. Available from: https://www.onepetro.org/conference-paper/NACE-01540

[10] M. Erfan, *Chloride removal in refineries*, PTQ Catalysis, 2011. Available from: http://www.digitalrefining.com/article/1000407,Chloride_removal_in_refineries_.html#.VX21js-eDRY

[11] M. Yari, *The 6 corrosive components that can be found in crude oil,* Corrosionpedia. Available from: "http://www.corrosionpedia.com/2/1424/corrosion/the-6-corrosive-components- that-can-be-found-in-crude-oil", (August 6, 2014).

[12] S.A. Lordo, *Primer on organic chlorides and their control*, Nalco, 2007. Available from: http://www.coqa-inc.org/docs/default-source/meeting-presentations/Lordo_Presentation.pdf

[13] V. Haensel, U.S. Patent 2,479,109, to UOP, 1949.

[14] V.A. Mazzieri, C.L. Pieck, C.R. Vera, J.C. Yori, J.M. Grau, *Effect of Ge content on the metal and acid properties of Pt-Re-Ge/Al_2O_3-Cl catalysts for naphtha reforming*, Appl. Catal. A-Gen **353** (2009) 93-100.

[15] *An introduction to petroleum refining and the production of ultra low sulfur gasoline and diesel fuel*, The International Council on Clean Transportation 2011. Available from: http://www.theicct.org/sites/default/files/publications/ICCT05_Refining_Tutorial_FINAL_R1.pdf

[16] http://webbook.nist.gov/cgi/cbook.cgi?ID=C12125029&Units=SI&Mask=F#ref-1

[17] http://www.webelements.com/electronegativity.html

[18] H.J. Werner, P. Rosmus, *Theoretical dipole moments of the HF, HCl, and HBr molecules*, J. Chem. Phys. **73** (1980) 2319.

[19] G.B. Hawkins, *Comparative performance of alternative chloride guard absorbents*, GBH Enterprises Ltd. Available from: "http://www.gbhenterprises.com/comparative%20performance%20of%20alternative%20chloride%20guard%20absorbents%20wsv.pdf"

[20] C. Nedez, U.S. Patent 6,589,494 B1, to IFP, 2003.

[21] R.T. Yang, *Adsorbents: Fundamentals and applications*, John Wiley & Sons, Inc.: New Jersey, 2003 (p. 1, 146-154)

[22] R.G. Mortimer, *Physical chemistry*, 3rd ed., Elsevier Inc, 2008 (p. 114-121).

[23] E. Worch, *Adsorption technology in water treatment: Fundamentals, processes, and modeling*, Walter de Gruyter & Co. KG: Berlin/Boston, 2012 (p. 1, 22).

[24] S. Deng, *Sorbent technology*, Encyclopedia of Chemical Processing Ed. by S. Lee, Marcel Dekker, Inc. New York, NY (2006) 2825-2845.

[25] A.B. de Haan, H. Bosch, *Industrial separation processes: Fundamentals*, Walter de Gruyter GmbH, Berlin/Boston, 2013 (p. 155-156).

[26] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, *Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk*, IOSR Journal of Applied Chemistry (IOSR-JAC), vol. 3, issue **1** (2012) p.38-45. Available from: http://iosrjournals.org/iosr-jac/papers/

[27] Z.K. Chowdhury, *Activated carbon: solutions for improving water quality*, American Water Works Association , 2013 (p.7-10)

[28] J. Daintith, *A dictionary of chemistry*, 6th ed., Oxford University Press, 2006. Available from: *http://www.oxfordreference.com/view/10.1093/acref/9780199204632.001.0001/acref-9780199204632-e-2408*

[29] A.T. Hubbard, *Encyclopedia of surface and colloid science*, vol. 1, Marcel Dekker, Inc., 2002 (p. 394-395).

[30] B. Sivasankar, *Engineering chemistry*, Tata McGraw-Hill, 2008 (p. 145-150).

[31] R.I. Masel, *Principles of adsorption and reaction on solid surfaces,* John Wiley & Sons, 1996 (p. 299-302). Available from:

[32] N.P. Stadie, *Synthesis and thermodynamic studies of physisorptive energy storage materials*, (Dissertation Ph.D.), California Institute of Technology. Available from: "http://resolver.caltech.edu/CaltechTHESIS:09092012-010239493"

[33] R.C. Bansal, M. Goyal, *Activated carbon adsorption*, Taylor & Francis Group, 2005 (p. 1, 121-122). Available from:

[34] C.H. Yang, *Statistical mechanical aspects of adsorption systems obeying the Temkin isotherm*, J. Phys. Chem. **97** (1993) 7097-7101.

[35] S. Brunauer, *The adsorption of gases and vapors,* vol. 1, Princeton University Press, 1943 (p. 27).

[36] M.C. Desjonqueres, D. Spanjaard, *Concepts in surface physics*, 2nd edition, Springer Science & Business Media, 1996 (chapter 6.4)

[37]http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Intermolecular_Forces/Lennard-Jones_Potential

[38] M. Shiraiwa et al., *The role of long-lived reactive oxygen intermediates in the reaction of ozone with aerosol particles,* Nature Chemistry **3** (2011) 291-295.

[39] J.M. Gottfried, *Adsorption and reaction of oxygen, carbon monoxide, and carbon dioxide on an Au(110)-(1x2) surface*, (Doctoral dissertation), Freie Universität Berlin, 2003.

[40] J.R. Philip, *Adsorption and geometry: the boundary layer approximation*, J. Chem. Phys. **67** (1977) 1732.

[41] S.D. Fraust, O.M. Aly, *Chemistry of water treatment. Second edition,* CRC Press LLC, 1998, p. 148-150.

[42] D.N. Jadhav, A.K. Vanjara, *Adsorption kinetics study: Removal of dyestuff effluent using sawdust, polymerized sawdust and sawdust carbon-II*, Indian J. Chem. Techn. **11** (2004) 42-50.

[43] B.K. Suyamboo, R.S. Perumal, *Equilibrium, thermodynamic and kinetic studies on adsorption of a basic dye by citrullus lanatus rind*, Iranica J. Ener. Environ. **3(1)** (2012) 23-34.

[44] M. Jain, *Competition science vision*, (1998, December), Issue 10, (p. 1419-1421). Available from: https://books.google.no/books?id=LOgDAAAAMBAJ&pg=PA1408&lpg=PA1408&dq=Competition+science+vision,+(1998,+December),+Issue+10&source=bl&ots=qvWwnSG7Pk&sig=llAp3JQfpJbBFEQCmvZSJEL_xIE&hl=en&sa=X&ved=0CB8Q6AEwAWoVChMIvpzCxvWPxgIVgZwsCh1eNA77#v=onepage&q&f=false

[45] A.D. McNaught, A. Wilkinson, *Compendium of chemical terminology,* 2nd ed., Oxford, 1997. Available from: http://goldbook.iupac.org/S06012.html

[46] M.A. Witek, *Techniques for the determination of sticking probability*, Spring 2001. Available from: http://www.cem.msu.edu/~cem924sg/MaggieWittek.pdf

[47] http://www.chem.qmul.ac.uk/surfaces/scc/scat2_3.htm

[48] G.A. Somorjai, Y. Li, *Introduction to surface chemistry and catalysis*, 2nd ed., John Wiley & Sons, 2010 (p. 358-361, 569)

[49] N.P. Stadie, *Synthesis and thermodynamic studies of physisorptive energy storage materials*, Dissertation (Ph.D.), California Institute of Technology, 2013.

[50] S. Fujita, K. Suzuki, T. Mori, Y. Shibasaki, *A new technique to remove hydrogen chloride gas at high temperature using hydrogrossular*, Ind. Eng. Chem. Res. **42** (2003) 1023-1027

[51] http://www.zeotec.co.in/

[52] *Particle size and shape of catalyst supports*, Horiba Scientific. Available from: "http://www.horiba.com/scientific/products/particle-characterization/applications/catalyst-supports/".

[53] I. Chorkendorff, J.W. Niemantsverdriet, *Concepts of modern catalysis and kinetics*, WILEY-VCH Verlag GmbH & Co., 2003, (p. 193, 205).

[54] S.J. Park, S.Y. Jin, *HCl removal using activated carbon fibers electroplated with silver*, Carbon **42** (2004) 2113-2130.

[55] L. Micoli, G. Bagnasco, M. Turco, *HCl removal from biogas for feeding MCFCs: Adsorption on microporous materials*, Int. J. Hydrogen Energ. **38** (2013) 447-452

[56] B.J. Kim, H. Park, S.J. Park, *Toxic gas removal behaviors of porous carbons in the presence of Ag/Ni bimetallic clusters*, Bull. Korean Chem. Soc. **29(4)** (2008) 782

[57] M.E. Hodson, *Measurements of internal and external surface area in feldspars - implications for mineral dissolution studies*, Mineralogical magazine, vol. 62A. Available from: "http://www.minersoc.org/pages/Archive-MM/Volume_62A/62a-1-634.pdf".

[58] M.F.J. Hochella, J.F. Banfield, *Chemical weathering of silicates in nature: a microscopic perspective with theoretical considerations. In Chemical Weathering Rates of Silicate Minerals (eds. A.F. White and S.L. Brantley),* Mineralogical Society of America, Washington DC, vol.31, (p. 353-406).

[59] M.T. Lee, Z.Q. Wang, J.R. Chang, *Activated-carbon-supported NaOH for removal of HCl from reformer process streams*, Ind. Eng. Chem. Res. **42** (2003) 6166-6170.

[60] B.K. Kim, S.K. Ryu, B.J. Kim, S.J. Park, *Roles of acid-base interactions in hydrogen chloride removal by activated carbon fibers*, Ind. Eng. Chem. **12** (2006) 121-126.

[61] S.K. Khanna, N.K. Verma, B. Kapila, *MCQ's in chemistry,* 2nd ed., Golden Bells, (p. 200).

[62] B.K. Sharma, *Objective pre engineering chemistry*, 6th ed., 2002 (p. 145).

[63] S.Suresh, S. Sundaramoorthy, *Green chemical engineering: An introduction to catalysis, kinetics and chemical processes*, Taylor & Francis, 2015, (p. 83).

[64] F.V. Molina, *Soil colloids: Properties and ion binding*, Taylor & Francis Group, 2014, (p. 76).

[65] A.M. Fonseca, J.J. Órfão, R.L. Salcedo, *Dry scrubbing of gaseous HCl with solid lime in a cyclone reactor at low temperatures*, Ind. Eng. Chem. Res. **40** (2001) 304-313

[66] B.K. Gullett, W. Jozewicz, L.A. Stefanski, *Reaction kinetics of Ca-based sorbents with HCl*, Ind. Eng. Chem. Res. **31** (1992) 2437-2446

[67] M.Li, H. Shaw, C.L. Yang, *Reaction kinetics of hydrogen chloride with calcium oxide by Fourier transform infrared spectroscopy*, Ind. Eng. Chem. Res. **39** (2000) 1898-1902

[68] T.J. Bandosz, *Activated carbon surfaces in environmental remediation*, 1st ed., Elsevier, 2006 (p. 78).

[69] B. Fried, J. Sherma, *Thin-layer chromatography*, 4th ed., Marcel Dekker, 1999 (p. 27).

[70] A.J. Downs, *Chemistry of aluminium, gallium, indium and thallium*, Chapman & Hall, 1993 (p. 282).

[71] Z.Sun, F.C. Yu, F. Li, S. Li, L.S. Fan, *Experimental study of HCl capture using CaO sorbents: Activation, deactivation, reactivation and ionic transfer mechanism*, Ind. Eng. Chem. Res. **50** (2011) 6034-6043

[72] M. Daoudi, J.K. Walters, *The removal of hydrogen chloride from hot gases using calcined limestone*, Management of hazardous and toxic waste in the process industries, Elsevier, London, 1987.

[73] T. Takase, N. Hayashi, Y. Shioya, K. Fujiwara, M. Ohashi, US 6,432,374, to Süd-Chemie Catalysts Japan and Japan Energy Corporation (JP), 2002.

[74] J.P. McWilliams, M.I. Nemet-Mavrodin, C.T. Sigal, R.C. Wilson, Jr., US 4,721,824, to Mobil Oil Corporation (N.Y.), 1988.

[75] R.W. La Hue, C.B. Hogg, US 3,935,295 A, to Catalysts and Chemicals Inc., 1976.

[76] T. Kameda, T. Yoshioka, T. Hoshi, M. Uchida, A. Okuwaki, *Treatment of hydrochloric acid with magnesium-aluminum oxide at ambient temperatures*, Sep. Purif. Technol. **51** (2006) 272-276.

[77] T. Kameda, N. Uchiyama, K.S. Park, G. Grause, T. Yoshioka, *Removal of hydrogen chloride from gaseous streams using magnesium-aluminum oxide*, Chemosphere **73** (2008) 844-847.

[78] T. Kameda, N. Uchiyama, T. Yoshioka, *Treatment of gaseous hydrogen chloride using Mg-Al layered double hydroxide intercalated with carbonate ion*, Chemosphere **81** (2010) 658-662.

[79] T. Kameda, N. Uchiyama, T. Yoshioka, *Treatment of gaseous hydrochloric acid with magnesium-aluminum oxide using batch operation*, Desalination **280** (2011) 424-427.

[80] J.A. Moulijn, M. Makkee, A. E. Van Diepen, *Chemical process technology,* 2nd ed., John Wiley & Sons, 2013 (p. 328).

[81] G. Neuss, *Chemistry for the IB diploma*, Oxford University Press, 2001 (p. 121).

[82] K. Tanabe, M. Misono, Y. Ono, H. Hattori, *New solid acid and bases. Their catalytic properties,* Kodansha Ltd., Tokyo, 1989 (p. 88).

[83] D.T. Lundie, A.R. Mcinroy, R. Marshall, J.M. Winfield, P. Jones, C.C. Dudman, S.F. Parker, C. Mitchell, D. Lennon, *Improved description of the surface acidity of the η-alumina*, J. Phys. Chem. B **109** (2005) 11592-11601.

[84] A.R. McInroy, D.T. Lundie, J.M. Winfield, C.C. Dudman, P. Jones, S.F. Parker, D. Lennon, *The interaction of alumina with HCl: An infrared spectroscopy, temperature-programmed desorption and inelastic neutron scattering study*, Catalysis Today **114** (2006) 403-411.

[85] D.D. Eley, *Advances in catalysis*, vol. 27, Academic Press, London, 1978 (p. 123-131).

[86] M. Blachman, U.S. Patent 6,200,544 B1, to Porocell Corporation, 2001.

[87] T. Lee, C.H. Ooi, R. Othman, F.Y. Yeoh, *Activated carbon fiber - the hybrid of carbon fiber and activated carbon*, Rev. Adv. Mater. Sci. **36** (2014) 118-136.

[88] M. Suzuki, *Activated carbon fiber: Fundamentals and applications*, Carbon **32** (1994) 577-586.

[89] M.T. Lee, Z.Q. Wang, J.R. Chang, *Activated-carbon-supported NaOH for removal of HCl from reformer process streams*, Ind. Eng. Chem. Res. **42** (2003) 6166-6170.

[90] H.L. Fleming, K.P. Goodboy, E.K. Saforo, U.S. Patent 4,762,537, to Aluminium Company of America, 1988.

[91] J. Guo, A.C. Lua, *Textural and chemical characterization of activated carbon prepared from oil-palm stone with H2SO4 and KOH impregnation*, Micropor. Mesopor. Mat. **32** (1999) 111-117

[92] H.V. Boening, *Plasma Science and Technology*, Cornell Press, New York (1982).

[93] R.C. Bansal, J.B. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker, New York (1998).

[94] C. Vagner, G. Finqueneisel, T. Zimny, P. Burg, B. Grzyb, J. Machnikowski, J.V. Weber, *Characterization of the surface properties of nitrogen-enriched carbons by inverse gas chromatography method*, Carbon **41** (2003) 2847.

[95] Z. Xu, J. Cai, B. Pan, *Mathematically modeling fixed-bed adsorption in aqueous systems*, J. of Zhejiang University- SCIENCE A, vol.**14**, no.3 (2013) 155-176.

[96] S. Gupta, B.V. Babu, *Kinetic modeling of fixed bed adsorption column*, Proceedings of International Symposium & 58th Annual Session of IIChE in association with International Partners (CHEMCON-2005), New Delhi, 2005.

[97] D.W. Sundstrom, H.E. Klei, *Wastewater treatment*, Prentice-Hall, Englewood Cliffs, NJ, 1979

[98] E. del Rio, D. Gaona et al. *Speciation-controlled incipient wetness impregnation: A rational synthetic approach to prepare sub-nanosized and highly active ceria-zirconia supported gold catalysts,* Journal of Catalysis **318** (2014) 119-127.

[99] http://www.norpro.saint-gobain.com/uploadedFiles/SGnorpro/Documents/CatalystCarriers-TypicalProperties-pf.pdf

[100] D.M. Ruthven, *Principles of adsorption and adsorption processes*, John Wiley & Sons, 1984 (p.199-200).

[101] H.S. Fogler, *Elements of chemical reaction engineering*, 4th ed., Pearson Education, 2006 (p.813-828).

[102] P. Zemek, J. Van Gompel, S. Plowman, *Ppm-level HCl measurements from cement kilns and waste incinerators by FTIR spectroscopy*, MIDAC Corporation. Available from: http://www.midac.com/files/AP-212.pdf