

Types of carbon adsorbents and their production

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1. TYPES OF CARBONS AND THEIR STRUCTURE

Carbon materials are mainly composed of the element carbon. Because of its atomic structure ($1s^2, 2s^2, 2p^2$) this element has unique bonding possibilities, both with other elements and with itself. Depending on the type hybridization of the carbon atoms these are able to bond with other carbon atoms, giving rise to three major* allotropic forms of carbon [1]:

- Diamond is a rigid and isotropic 3D-structure in which each carbon atom shares four σ -bonds with four other neighbouring carbon atoms, that form a cubic structure (sp^3 -based structure). It has the highest atomic density of any solid and is also the hardest material with the highest thermal conductivity and melting point.
- Graphite is a layered structure in which the graphene layers (single graphite plane) are formed by atoms of carbon bonded by σ - and π -bonds to another three neighbouring carbon atoms (sp^2 -based structure). The graphite planes tend to exhibit a parallel alignment which is maintained by dispersive and Van der Waals forces. This leads to a high degree of anisotropy. Graphite (in plane) has an even higher thermal conductivity than diamond and exhibits a good electrical conductivity.
- Fullerenes are three-dimensional carbon structures where the bonds between the carbon atoms are bent to form an empty cage of sixty (C_{60}) or more carbon atoms. This is possible due to the fact that re-hybridisation occurs, resulting in a $sp^{2+\epsilon}$ form, which is intermediate between sp^2 and sp^3 [2].

On an atomic scale, the majority of carbons exhibit the allotropic form of graphite i.e. a sp^2 -based structure, while diamond-like carbons, fullerenes and their derivatives, such as nanotubes, represent a shorter variety of carbon forms. However, depending on the degree of

* There are also other less abundant allotropic forms of carbon like carbynes (sp -based hybridization) or rhombohedral graphite [1].

crystallographic order in the third direction (c-direction), carbons based on the allotropic form of graphite can be classified into **graphitic** carbons (which have a measurable crystallographic order in this direction irrespective of the presence of structural defects) and **non-graphitic** carbons (without any measurable crystallographic order in the c-direction direction apart from a more or less parallel stacking) carbons. [3].

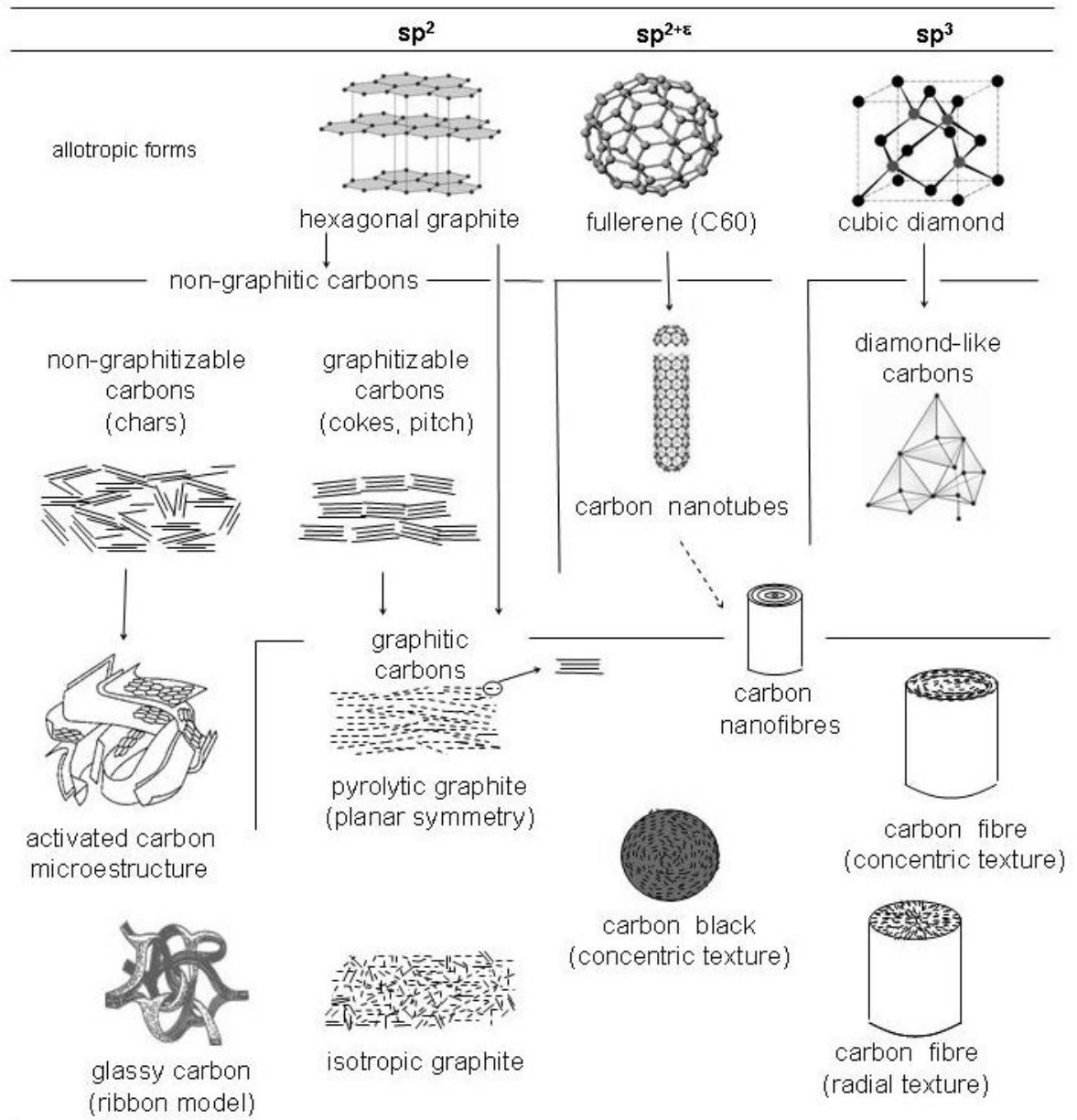


Fig. 1. Major allotropic forms of carbon and a schematic representation of some of the carbon structures derived from these forms [4, 5]

Non-graphitic carbons can in turn be divided into **graphitizable** and **non-graphitizable** carbons. Thus, a graphitizable carbon is “a non-graphitic carbon which upon graphitization (heat treatment) is converted into graphitic carbon”, while a non-graphitizable carbon is “a non-graphitic carbon which cannot be transformed into graphitic carbon by high-temperature treatment up to 3300 K under atmospheric pressure or a lower pressure” [2].

Moving up from nano-scale to micro-scale, carbons exhibit very different structures. Some of these microstructures are arranged in preferential directions, like synthetic graphite or graphitized carbon fibres, while disordered microstructures are characteristic of chars or activated carbons. Such a wide variety of possible structures gives rise to a large amount of different types of carbons. Figure 1 shows a schematic representation of some of these carbon structures.

Powder (particle size lower than $100 \cdot 10^{-6}$ m) and granular (including extruded and pelletized) activated carbons are typical carbon adsorbents. These are non-graphitic, non-graphitizable carbons with a highly disordered microstructure. Other forms of carbons are also used as adsorbents such as activated carbon fibres, fabrics and felts prepared from a wide variety of precursors including coal, petroleum pitch, viscose or rayon. Moreover, exfoliated graphite can also be used to adsorb heavy oils [6]. The use of carbon nanotubes for hydrogen storage is also a current subject of study.

2. HISTORICAL BACKGROUND OF THE ACTIVATED CARBONS

The use of carbon extends so far back in time that its origin is impossible to determine exactly. Prior to the use of what we call today activated carbon (which has a highly developed porous structure), either wood char, or coal char or simply a partially devolatilized carbonaceous material was employed as an adsorbent. The first recorded case dates back to 3750 BC, when both the Egyptians and Sumerians used wood char for the reduction of copper, zinc and tin ores in the manufacture of bronze, and also as a smokeless fuel [7]. In 2650 BC, the Egyptians used bonechar to wallpaint Perneb's grave. The first proof of the medicinal use of carbon was found in Thebes (Greece), in a papyrus document from 1550 BC [8]. Later on, Hippocrates (around 400 BC) recommended that water should be filtered with woodchar prior to consumption, in order to eliminate bad taste and odor and to prevent several diseases, including epilepsy, chlorosis and anthrax. In relation to the treatment of ancient drinking water, recent studies indicate that on Phoenician ships drinking water was stored in charred wooden barrels from 450 BC, a practice which continued until the 18th century as a means of prolonging the supply of drinking water on transatlantic voyages.

Nevertheless, the first reported application of activated carbons as a gas phase adsorbent did not take place until as late as 1793 AD, when Dr. D.M. Kehl applied woodchar in order to mitigate the odours emanating from gangrene. The above gentleman also recommended filtering water with woodchar.

The first application of activated carbon in the industrial sector took place in England in 1794, when it was used as a decolorizing agent in the sugar production industry, this event

marking the beginning of research with activated carbons in liquid phase. This application remained a secret until 1812 (18 years), when the first patent appeared in Great Britain, although several sugar refineries were already using woodchar as a decolorizing agent before 1808. In 1811, it was proved that bone char was more effective than woodchar and its regeneration became the established objective. The first patent for the thermal regeneration of activated carbon dates from 1817, and a continuous process for manufacturing and regenerating bone char was developed in Germany in 1841.

The first large scale gas-phase application took place in the mid 19th century. In 1854, the Mayor of London ordered the installation of wood char filters in all the sewer ventilation systems to remove nasty odours, while in 1872 gas masks with carbon filters were used in chemical industries to prevent mercury vapours from being inhaled.

The term 'adsorption' was first used in 1881 by Kayser to describe the uptake of gases by chars. At about the same time, activated carbon material, as it is known nowadays, was discovered by R. von Ostrejko, who is considered the father and/or inventor of activated carbon [9]. In 1901, he patented two different methods of producing activated carbons:

- The carbonization of lignocellulosic materials with metal chlorides (the basis of chemical activation).
- The mild gasification of chars with steam or carbon dioxide at red temperatures (thermal or physical activation).

At around this time, von Ostrejko also patented specific equipment and utilities for producing activated carbons. In 1910, Wijnberg and Sauer acquired the patent rights, and were the first to apply activated carbons to the sugar industry (Norit White Sugar Company), referring to these carbons as 'noir épuré', 'eponit' or 'norit', although the carbons were purchased from Stettiner Spritt Werke and Erste Österreichische Ceserin Werke AG in Stockerau [10]. Later, the company decided to produce its own carbons from peat during the First World War in Zaandam, under the name of NV Nederlandse NORIT Maatschappij (Dutch NORIT Company). On the other hand, the first commercial chemically activated carbon (Carboraffin) was produced in Aussig (the Czech Republic) in 1914, using sawdust as raw material and $ZnCl_2$ as activating agent.

The First World War stimulated the development of both the production and application of activated carbons. The use of poisonous gases by the German army against the French, British and Russians on different fronts, posed a severe problem for the allies, and as a consequence, there was an urgent need for gas mask development. Nikolai Zelinski, a professor at Moscow University was the first to suggest packing activated carbons inside a canister fitted to a gas mask [11]. A bit later, an intensive research program was carried out in the USA with the development of coconut-shell based granular activated carbons that could be packed inside a canister, with the two fold objective of removing poisonous gas and of offering a low pressure drop.

Without doubt, the First World War was the starting point of activated carbon development, when it was used not only in the white sugar industry, but also as an adsorbent

for water treatment and the adsorption and removal of vapours in gas phase. The rapid development of society over the 20th century, promoted by the medical and scientific improvements as a consequence of the industrial revolution of the previous century, has also affected the use of activated carbon. Indeed the production and utilization of activated carbon has increased with every decade, specially in the second half of the last century due to the stricter environmental regulations regarding both water resources, clean gas application and economic recovery of valued chemicals. In the last thirty years, the use of activated carbon as a metal catalyst support instead of carbon blacks has also been widespread [12].

The study of activated carbons, or carbon adsorbents, is included in what is commonly called Science and Technology of Carbon Materials, where a variety of carbon based materials are employed (such as the above mentioned carbon blacks, nanotubes, etc). Although the development and use of carbon adsorbents have brought enormous benefits to mankind, the words of Professor Harry Marsh (1997) [13] claiming that “*Activated carbon is the Cinderella of the Carbon family, (...) and after purifying tonnes of sugar, cleaning up oceans of water, and enormous amounts of food, (...), they were never taken to the Ball*” cannot be ignored. Nevertheless, in recent years a growing interest has been shown in Activated Carbon Fibres (ACF), derived from the carbon fibers of viscose rayon (1966), Saran (1970), phenol-formaldehyde resin (1980) or coal pitch (1985) [14].

3. PHYSICAL AND CHEMICAL PROPERTIES OF ACTIVATED CARBONS

Carbon adsorbents have a porous carbon structure, which contains small amounts of different heteroatoms such as oxygen and hydrogen. Some activated carbons also contain variable amounts of mineral matter (ash content) depending on the nature of the raw material used as precursor. The porous structure is perhaps the main physical property that characterizes activated carbons. This is formed by pores of different sizes which according to IUPAC recommendations [15] can be classified into three major groups (see Figure 2):

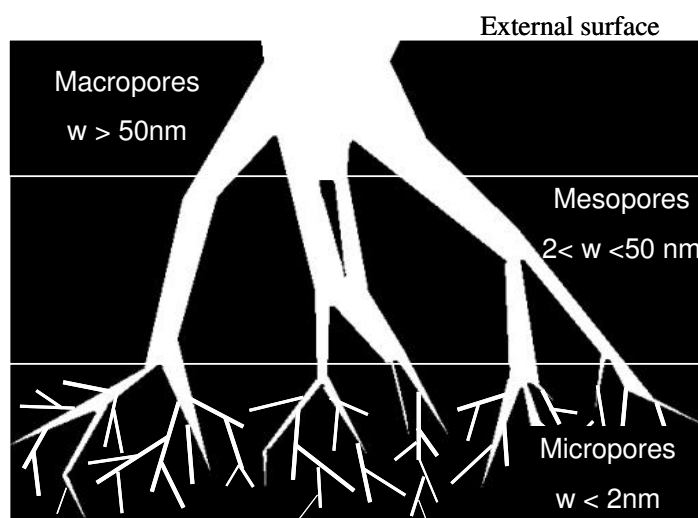


Fig. 2. Schematic representation of the pore network of a carbon adsorbent

- Micropores with a pore width of less than $2 \cdot 10^{-9}$ m.
- Mesopores with widths from 2.0 to $50 \cdot 10^{-9}$ m.
- Macropores with a pore width larger than $50 \cdot 10^{-9}$ m.

Furthermore, the presence or absence of surface groups, formed by heteroatoms (atoms different to the carbon atom), that may bond themselves to the carbon atoms at the edges of the basal planes gives rise to carbons with different chemical properties. The physical and chemical properties are of great importance for the behaviour of carbon adsorbents and they will be discussed in depth in other chapters of this book. We would like, however, to outline here some basic concepts and provide an overall view of the importance that these properties have for the adsorption processes.

3.1. The importance of the porous texture

The structure of the carbon skeleton can be considered as a mixture of graphite-like crystallites and non-organized phase composed of complex aromatic-aliphatic forms. The crystallites are composed of a few (about three) parallel plane layers of graphite, the diameter of which are estimated to be about $2 \cdot 10^{-9}$ m, or about nine times the width of one carbon hexagon [16]. The regular array of carbon bonds on the surface of the crystallites is disrupted during the activation process, yielding relative free valences. The crystallites are randomly oriented and extensively interconnected. The structure of an activated carbon may be visualized as a stack of poorly developed aromatic sheets (crystallites), distributed and cross-linked in a random manner, separated by disorganized carbonaceous matter and inorganic matter (ash) derived from the raw material. The anisotropic crystallite alignment is associated with the presence of voids. During the activation the spaces between the crystallites become cleared of less organized carbonaceous matter and, at the same time, some of the carbon is removed from the crystallites. The resulting channels through the graphitic regions and the interstices between the crystallites of the activated carbon, together with fissures inside and parallel to the graphitic planes, make up the porous structure which usually has a large surface area. These range over several sizes and are therefore classified into the three groups mentioned above.

In the different adsorption processes, both in gas and liquid phase, the molecules or atoms (adsorbable) are fixed (adsorbed) on the carbon (adsorbent) surface by physical interactions (electrostatic and dispersive forces) and/or chemical bonds. Therefore, a relatively large specific surface area is one of the most important properties that characterize carbon adsorbents. The surface of the activated carbons consists mainly of basal planes and the edges of the planes that form the edges of microcrystallites.

Adsorption capacity related parameters are usually determined from gas adsorption measurements. The specific surface area is calculated by applying the Brunauer-Emmett-Teller (BET) equation [17] to the isotherms generated during the adsorption process. The adsorption of N_2 at 77 K or CO_2 at 273 K are the most commonly used to produce these isotherms. The BET theory is based upon the assumption that the monolayer is located on

surface sites of uniform adsorption energy and multilayer build-up via a process analogous to the condensation of the liquid adsorbate. For convenience, the BET equation is normally expressed in the form:

$$\frac{p/p^0}{n(p^0 - p)} = \frac{1}{nC} + \frac{C-1}{n_m C} \frac{p}{p^0} \quad \text{where } C = \exp\left(\frac{q_1 - q_L}{RT}\right) \quad (1)$$

which requires a linear relationship between $(p/p^0)/(n(p^0-p))$ and p/p^0 , from which the monolayer capacity, n_m (mmol g⁻¹), can be calculated. In activated carbons the range of linearity of the BET plot is severely restricted to the p/p^0 range of 0.05-0.20. The alternative form of linearization of the BET equation employed by Parra and coworkers [18] appears to be more convenient for a microporous solid since the choice of the appropriate experimental interval is free of ambiguity.

The BET equation, however, is subject to various limitations when applied to microporous carbons. Thus, constrictions in the microporous network may cause molecular sieve effects and molecular shape selectivity. Diffusion effects may also occur when using N₂ at 77 K as the adsorbate since at such low temperatures the kinetic energy may be insufficient to penetrate all the micropores. For this reason adsorption of CO₂ at higher temperatures (273 K) is also used. CO₂ and N₂ isotherms are complementary. Thus, whereas from the CO₂ isotherm micropores of up to approximately 10⁻⁹ m width can be measured, the N₂ can be used to test larger pores. Despite these limitations the BET surface area is the parameter most commonly used to characterize the specific surface area of carbon adsorbents.

On the basis of volume-filling mechanism and thermodynamic considerations, Dubinin and Radushkevich [19] found empirically that the characteristic curves obtained using the Potential Theory for adsorption on many microporous carbons could be linearized using the Dubinin-Radushkevich (DR) equation,

$$V = V_0 \exp\left(-\frac{\varepsilon}{\beta E}\right)^2 \quad (2)$$

where V_0 is the micropore volume, E is an adsorption energy, β is an adsorption characteristic constant dependent on the adsorbate, and $\varepsilon = RT \ln (p^0/p)$ is the adsorption potential at the temperature T (K). For some microporous carbons the DR equation is linear over many orders of magnitude of pressure. For others, however, deviations from the DR equation are found. For such cases the Dubinin-Astakhov equation has been proposed in which the exponent 2 of the DR equation is replaced by a third adjustable parameter, n , where $1 < n < 3$.

Both the BET and the Dubinin models are widely thought to adequately describe the physical adsorption of gases on solid carbons. BET surface areas from many microporous carbons range from 500 to 1500 m² g⁻¹. However, values of up to 4000 m² g⁻¹ are found for some super-activated carbons and these are unrealistically high.

The relatively high values of the surface areas of activated carbons are mainly due to the contribution of the micropores and most of the adsorption takes place in these pores. At least

90-95% of the total surface area of an activated carbon may correspond to micropores. However, meso- and macropores also play a very important role in any adsorption process since they serve as the passage through which the adsorbate reaches the micropores. Thus, the mesopores, which branch off from the macropores, serve as passages for the adsorptive to reach the micropores. In such mesopores capillary condensation may occur with the formation of a meniscus in the adsorbate. Although the surface area of the mesopores is relatively low in most activated carbons, some may have a well developed mesoporosity ($200 \text{ m}^2 \text{ g}^{-1}$ or even more).

In addition, depending on the size of the adsorbate molecules, especially in the case of some organic molecules of a large size, molecular sieve effects may occur either because the pore width is narrower than the molecules of the adsorbate or because the shape of the pores does not allow the molecules of the adsorbate to penetrate into the micropores. Thus, slit-shaped micropores formed by the spaces between the carbon layer planes are not accessible to molecules of a spherical geometry, which have a diameter larger than the pore width. This means that the specific surface area of a carbon is not necessarily proportional to the adsorption capacity of the activated carbon. Pore size distribution, therefore, is a factor that cannot be ignored.

The suitability of a given activated carbon for a given application depends on the proportion of pores of a particular size. In general highly microporous carbons are preferred for the adsorption of gases and vapours—and for the separation of gas molecules of different dimensions if the carbon possesses a suitable distribution of narrow size pores (molecular sieves)—while well developed meso- and macroporosity is necessary for the adsorption of solutes from solutions.

3.2. The importance of the surface chemistry

It has already been pointed out that a high surface area and an adequate pore size distribution are necessary conditions for a carbon adsorbent to perform well in a particular application. However, there are many examples of carbons with similar textural characteristics, which show a very different adsorption capacity with the same adsorbate [12]. The reason for these different behaviours is that an adequate porous texture is a necessary but not a sufficient condition for the optimization of the adsorption capacity of activated carbons. The nature and amount of surface groups that may be present on the carbon surfaces must also be taken into account.

Carbon atoms located at the edges of the basal planes are unsaturated carbon atoms, which possess unpaired electrons. These sites are usually bonded to heteroatoms giving rise to surface groups. Among these groups, oxygen-containing surface groups are by far the most common in carbons. In particular, activated carbons (non-graphitizable carbons) have a relatively large edge area, which results in a strong propensity for oxygen chemisorption. Thus, molecular oxygen can dissociate into atoms that react chemically with atoms of carbon to form oxygen surface compounds. This oxidation process is particularly significant as the temperature of the reaction increases, but also at room temperature for carbons previously

treated at high temperatures, which present a highly reactive surface. Oxygen-containing surface groups are not only formed by reaction with oxygen but can also result from reaction with many other oxidizing gases such as ozone, nitrous oxide, carbon dioxide, etc. and with oxidizing solutions like nitric acid, hydrogen peroxide, etc. Thus, the surface chemistry of activated carbons can be tailored by oxidation with different agents in order to create oxygen functionalities or by heat treatment in order to remove them either selectively or completely depending on the temperatures used [20]. Figure 3 summarizes the most important types of surface groups that may be present on carbon surfaces.

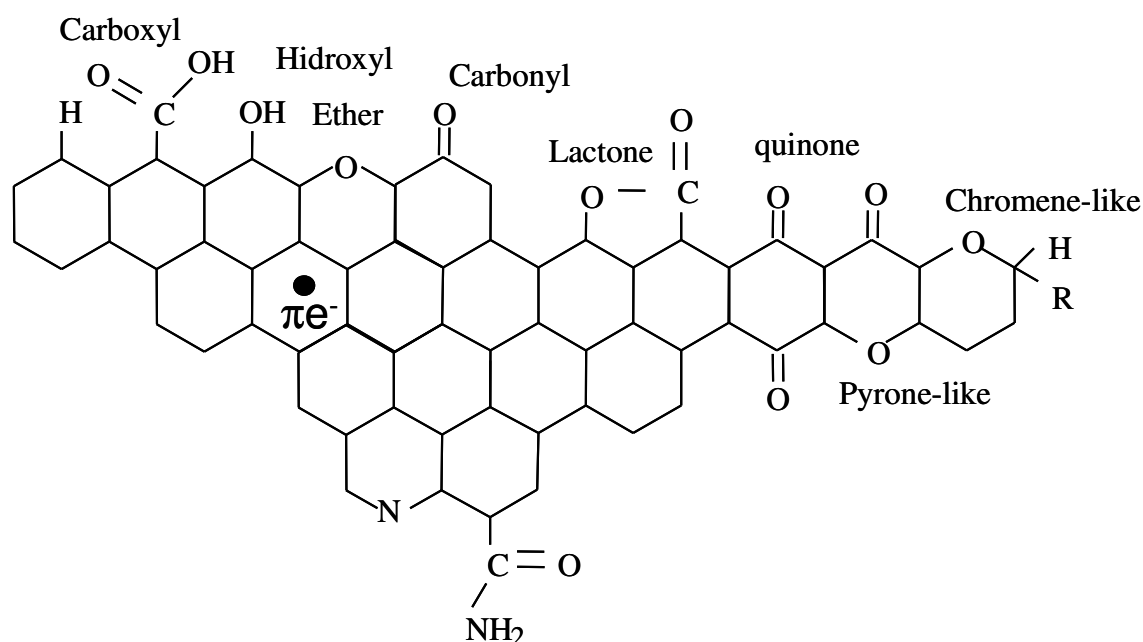


Fig. 3. The most important types of surface groups that may be found on a carbon surface

As mentioned above, oxygen-containing groups are the most common and abundant, but hydrogen is also found combined with edge carbon atoms. In addition, treatments with ammonia, melamine or urea can be used to introduce nitrogenated functionalities, which confer special characteristics on the activated carbons. Of course not all of these functionalities are present at the same time on a carbon. The nature and amount of the different surface oxygen-containing carbon groups on a carbon surface may vary depending on the oxidation conditions.

The surface sites associated with functional groups represent a small proportion of the total surface area. However, small variations in the chemical nature of an activated carbon may produce important changes in its adsorption capacity. The importance of the surface groups lies in the fact that their presence or absence can have an important effect on the interaction of carbons with different adsorbates. Two principal effects must be considered.

One is the modification of the hydrophobic/hydrophilic character of the carbon. Carbons are, in general, of a hydrophobic nature. However, the presence of polar oxygen-containing

surface groups causes an increase in hydrophilicity since water molecules can form hydrogen bonds with the oxygen atoms of the carbon surface. These molecules may in turn form new hydrogen bonds with new water molecules. The mechanism is schematized in Figure 4. This effect is of particular importance in the preparation of carbon-supported catalysts from aqueous solutions, where the wettability of the carbon will determine the degree of impregnation of the carbon surface by the solution that contains the catalyst to be supported [12]. In the case of the adsorption of the compounds in a gas stream, the presence of oxygen functionalities can be detrimental since the adsorption of moisture (water molecules) may block the access of the adsorbate to a part of the micropores, thereby impairing the adsorption capacity of the activated carbon.

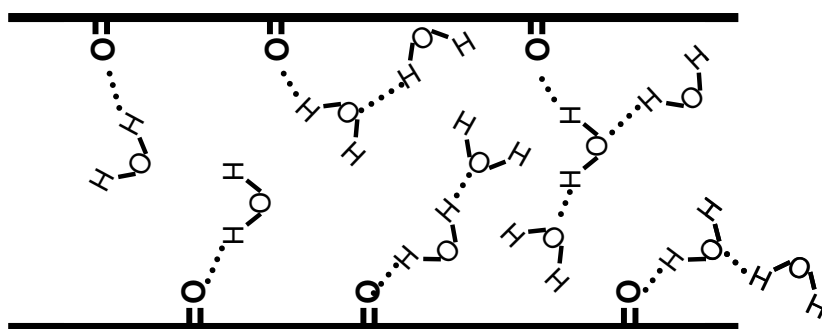


Fig. 4. Increase in the hydrophilic character of a carbon surface as a consequence of the presence of oxygen-containing surface groups

The other important effect of the surface groups is the influence that they have on the acidic or basic character of the carbons. Activated carbons are amphoteric by nature. That is, they have acidic and basic sites that coexist on their surface. Thus, the carboxyl, hydroxyl and lactone groups behave as acidic groups, if the pH of the medium is higher than the pK_a of these groups (basic medium). However, the nature of the basic sites of the activated carbons is more controversial. It is generally admitted that pyrone-like and chromene-like groups [21], among the oxygen functionalities, and the delocalized π -electrons of the basal planes [22] are the main basic sites that occur on a carbon surface, although some nitrogen-containing functionalities can also behave as basic sites (these less common functionalities are not discussed in this introductory chapter). However, whether basic oxygen-containing groups have a greater impact on carbon basicity than the delocalized π -electrons of the basal plane is an issue that can only be resolved after an evaluation of the relative concentration of the different types of groups and their strengths as bases (pK_a) on the carbon surface [20]. Unfortunately these two values cannot be easily determined. By the same token, the overall acidity or basicity of a given carbon depends on the concentration and the strength as acids or bases of the acidic and/or basic sites on the carbon surface. Thus, if the acidic groups are more numerous or their overall acidic strength is higher than that of the basic groups the

carbon will be of a basic nature and viceversa. Another factor to be considered is the pH of the medium in relation to the point of zero charge (pH_{PZC}) of the activated carbon. Thus, if the $pH > pH_{PZC}$, acidic functionalities will dissociate, releasing protons into the medium and leaving a negatively charged surface on the carbon. On the other hand, if the $pH < pH_{PZC}$, basic sites combine with protons from the medium to leave a positively charged surface. This behaviour is schematically represented in Figure 5.

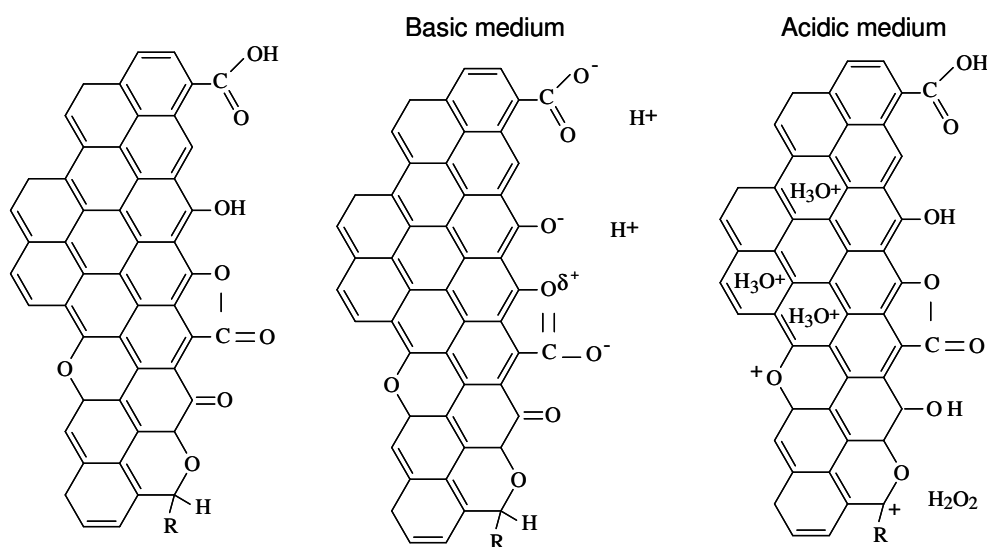


Fig. 5. Schematic representation of the acidic and basic behaviour of the oxygen-containing surface groups and delocalized π -electrons of the basal plane

In the light of the above considerations, the interactions and the adsorption capacity of the activated carbons can be optimised by modifying the surface chemistry of the carbon (and/or the pH of the medium, when this is possible). Thus, in a simplistic approach, basic carbons are preferable for adsorbing acidic molecules while acidic carbons will perform better for the adsorption of basic compounds. Moreover, the adsorption of cations will be favoured (by electrostatic forces) if the carbon surface is negatively charged, while the adsorption of anions will be enhanced on a positively charged surface.

4. PRODUCTION OF CARBON ADSORBENTS

Activated carbons were the first adsorbents to be developed. As stated in previous sections, activated carbons are produced from a solid carbonaceous based material, which is non-graphitic and non-graphitizable, and has an initial isotropic structure. The precursor is transformed or 'activated' by means of medium to high temperature treatments, which remove solid mass, and at the same time, create pores where the removed mass was previously located. The common properties of activated carbons and other kinds of carbon adsorbents is their well developed pore network, and the similar ways in which they are

produced. In this section details of activated carbon production (raw materials, chemical process, industrial reactors, etc.) will be presented.

4.1. Raw materials

Since an activated carbon is structurally a non-graphitic carbonaceous material, almost any carbonaceous solid material can be converted into activated carbon. There are, therefore, plenty of possible raw materials such as wood, lignocellulosic biomass, peat, lignite and coals that can be used to make activated carbon. However, there are some limitations. Since activated carbon is disordered and isotropic, the raw material must not be allowed to pass through a fluid or pseudofluid state due to the fact that the solid structure tends to transform into an ordered structure. Consequently, coking coals are not an appropriate raw material, unless they are first treated with anti-coking processes (e.g. low-temperature preoxidation). Similarly, thermoplastic wastes are not a suitable raw material because they melt with increasing temperature, losing their initial shape and particle size. On the other hand, a stabilized solid char from a thermoset material does have the necessary characteristics of an appropriate raw material.

In practice, wood, coconut shells, fruit stones, coals, lignites, petroleum coke, etc. are all inexpensive materials with a high carbon content and a low inorganic content, and consequently, are suitable for use as an activated carbon precursor. The resulting properties of the product are dependent on the precursor, and consequently, the carbons can be tailored for selected applications. Furthermore, the resulting activated carbon properties are also influenced to a great extent by the activation treatment. Selection of the appropriate raw material is based on the following criteria [23]:

- Possibility of yielding a good activated carbon in terms of adsorption capacity, high density and hardness.
- Low in inorganic matter. The adsorption capacity is measured per mass unit, and since inorganic materials are non-porous, their presence reduces the adsorption capacity [24].
- Availability and cost. As with any other product, the price of the raw material affects the final cost, so a high availability is important to ensure stable prices. It should also be taken into account that there is a considerable mass loss in all the activation treatments, and the lower the product yield, the higher the cost. The product yields may vary considerably, and can be as low as 5-10% for wood-based carbons. Moreover, raw material availability obviously depends on the part of the world in which the plant is located.

Figure 6 shows the estimated world production of activated carbon per region and per precursor in 1993 [25]. Total production exceeded 350000 tonnes/year: coconut shells (34%), coal (31%) and wood (24%) these being the most important precursors. However, the raw materials used per world region shows a very different picture. In Europe, the raw material

most used was peat (36000 ton/year, 36% of total European production), whereas the production of coconut shell based carbon occupied fourth place with only 12% of the share. On the other hand, coconut based carbons led in Asia with over 60% of the share, North America occupying a position between Asia and Europe, with nearly the same production of coal, coconut and wood based activated carbons.

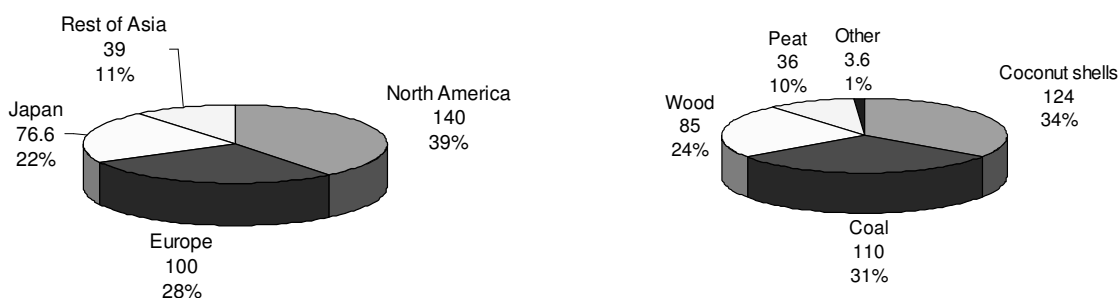


Fig. 6. 1993 world production of activated carbon per region and per precursor [25]. Production is given in kton/year

In 2002 the total production of activated carbon was estimated to be 750000 ton/year [26], which represents a rise of two times the level of production in less than 10 years. This change comes at a time when the production capacity is shifting from western industrialised countries to China and South-East Asia, where raw material, energy and labour costs are lower. By world regions, Asia is leading world production with 54% of the total share, followed by America with 32% and Europe with only 14%. By countries, Figure 7 shows the current world producers, where it can be seen that China manufactures 23% of the world production.

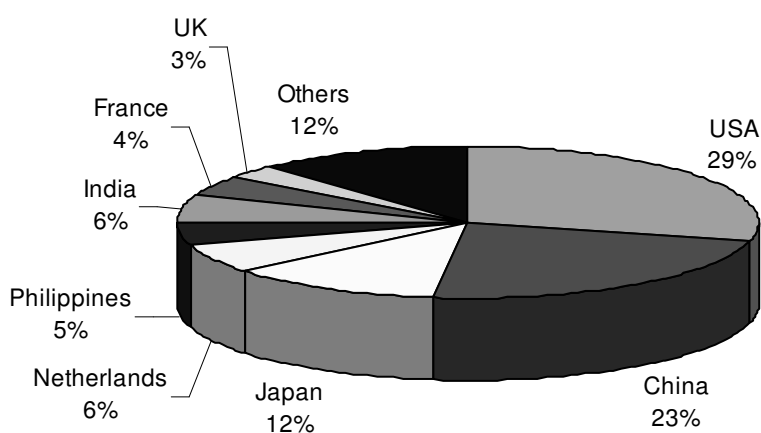


Fig. 7. World production capacity per leading country [26]

As stated above, the precursor is very important for both the activation process and the final properties of a given carbon adsorbent. As will be commented in section 4.2, the production methods can be grouped into i) physical, or more properly thermal activation, which consists in thermal devolatilization followed by char gasification with an oxidating agent, and ii) chemical activation, which consists basically in the inert carbonization of mixtures of the raw material with a chemical agent. When the raw material is subjected to thermal activation, the higher the volatile content of the raw material, the lower the yield. This type of treatment, however, gives rise to a more accessible micropore structure, thereby ensuring a higher and more homogeneous pore development. On the other hand, low volatile raw materials (such as anthracites or cokes) lead to a greater density and hardness. Most activated carbon materials are produced in either granular or powdered forms, depending on the final application. The type of raw material used also determines whether the activated carbon produced from it will be in powdered or granular form.

4.2. Thermal activation

There are many ways of producing activated carbon, and thousands of patents have been registered worldwide. Nevertheless, as mentioned in the previous section, all these production methods can be classified into two clearly defined groups:

- Thermal Activation (or physical activation). Generally (although not necessarily), this consists of two consecutive steps. The first step is thermal *carbonization* of the raw material, where devolatilization takes place, carried out at medium or high temperatures, to produce a char rich in carbon. The second step is *activation*, where the remaining char is partially gasified with an oxidizing agent (mostly steam) in direct fired furnaces. If both steps are carried out simultaneously, the process is called *direct activation*.
- Chemical Activation. This is carried out in a single carbonization stage. The raw material is first impregnated with appreciable amounts of a chemical agent (the usual chemical reagent vs. raw material ratios being around 1-4), and then heated up. The product must be washed to eliminate any excess chemical agent after carbonization. The thermal treatment temperature depends on what chemical agent is used. The most common are phosphoric acid, $ZnCl_2$ and alkaline hydroxides.

Thermal activation is generally divided into two thermally dependant steps, carbonization followed by activation. However, additional treatments are often applied. These are common industrial operations and are commented on below. The main scheme for activation production is shown in Figure 8.

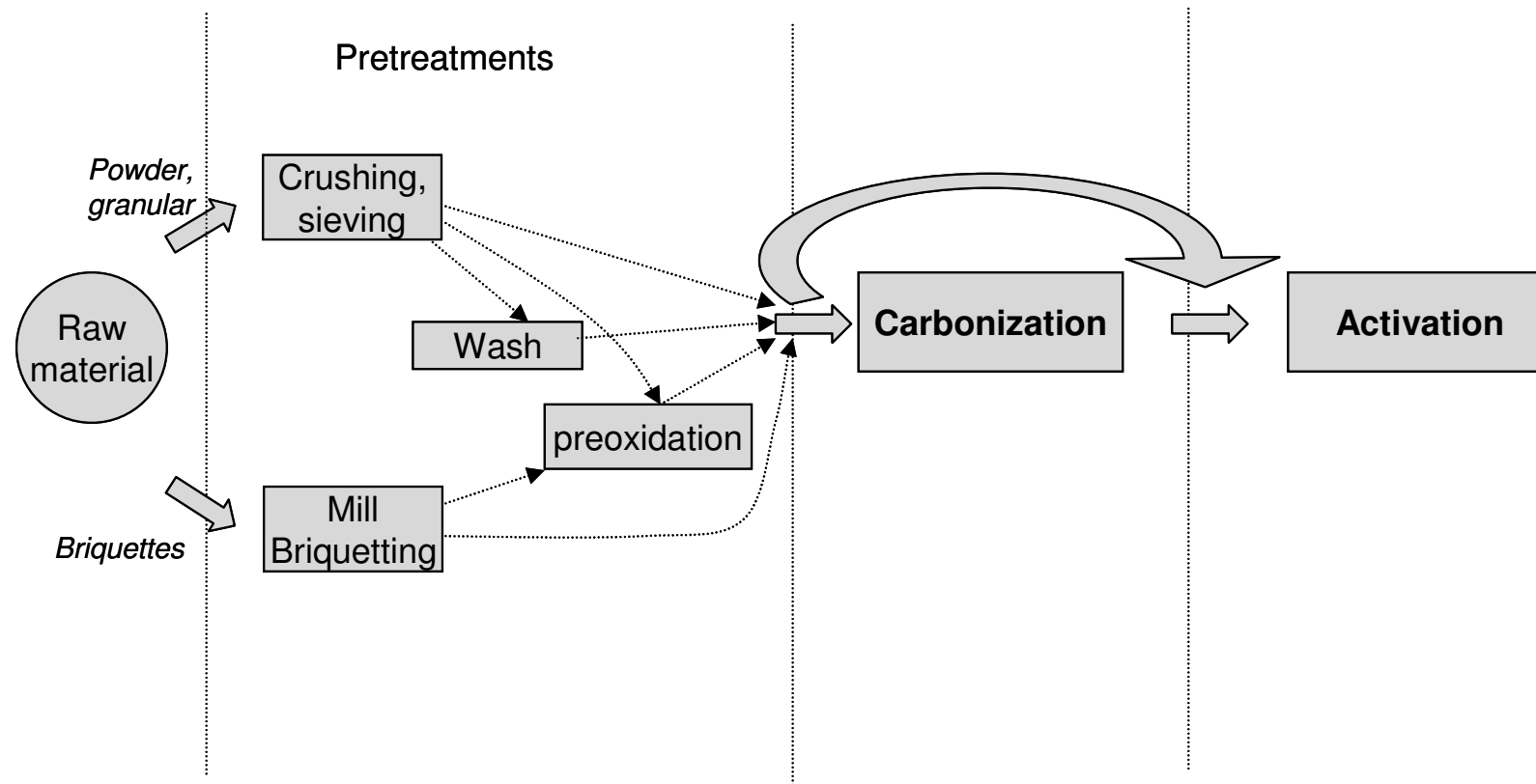


Fig. 8. General flowsheet for the production of thermal activated carbons

4.2.1. Pretreatments

The raw material will need some pretreatments prior to its activation. In the case of regular powdered or granular broken carbons, the raw material must first be prepared to the required particle size by crushing and sieving. Sometimes, a washing step is applied with water or acid in order to remove any dirt coming with the raw material and to reduce any mineral matter. If the raw material is a coking coal, preoxidation treatment is necessary: a long period of air-preoxidation at moderate temperatures (say 453-573 K), stabilizes the coal by creating crosslinkage within the coal structure, which prevents the fluid phase from occurring during carbonization [27].

Besides the powdered or granular carbons, the initial raw material is sometimes pulverized, briquetted and again crushed to an appropriate particle size. This treatment is normally applied to low volatile precursors (medium-high rank coals), where the meso and macropore network is not well developed in the carbonization step and the activating agent can diffuse poorly in the subsequent activation step. If a granular material with a well-developed internal porosity is required from these precursors, the coal must be finely pulverized and then briquetted. When the briquettes have been crushed, the material resembles the granules which have only been milled, but they have a well developed network of transport pores, so that the activated agent can diffuse easily to all the individual coal particles in the briquette. As an example, Figure 9 shows the meso and macropore size distribution of two bituminous coal based activated carbons, one of which has not been briquetted, whereas the other has. The pore size distribution was determined by mercury porosimetry. Figure 9 shows that for the briquetted carbon, there is a huge peak at pore sizes around 10^{-6} m, whereas the amount of pore volume distribution for the non-briquetted carbon is similar regardless of the pore size range. The peak is often called briquetted peak (or extrusion peak, if the carbon granules are produced by extrusion) and it is derived from the interparticle void volume among the pulverized particles of the briquettes.

4.2.2. Carbonization

As Figure 8 shows, pre-treatment is followed by the *carbonization* step. This step is usually critical in the overall production of activated carbons, because it is during this step when the micropore structure starts to form. The terms pyrolysis and carbonization are often used without distinction, and both processes are almost identical. However, there are differences in the objectives of each process. Both pyrolysis and carbonization refer to the thermal degradation of a carbonaceous material (coal, lignite, wood, polymer, etc) in an inert atmosphere, where the total or partial devolatilization of the raw material takes place. The difference is that, in pyrolysis, it is the gaseous and volatiles compounds evolved from the solid that are the objective of the process, and all process conditions (temperature, residence time, etc.) are focused on producing gaseous compounds (e.g. pyrolysis conditions to favour the light olefin fraction), regardless of the final char residue. On the other hand, in a carbonization process, thermal treatment focuses on the final properties of the char (e.g. porous texture, hardness, density, etc), regardless of the volatile compounds evolved.

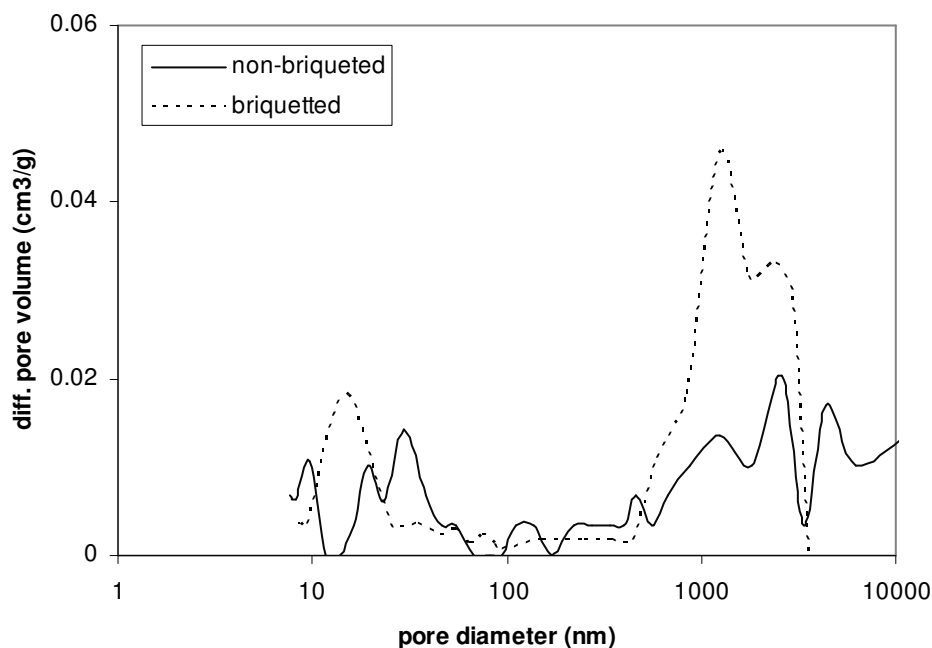


Fig. 9. Mercury porosimetry of a briquetted and a non-briquetted based granular activated carbon

A scheme of the carbonization (or pyrolysis) of a carbonaceous material is shown in Figure 10. The starting material, based on an organic macromolecular structure, decomposes during the thermal treatment to yield:

- A gaseous fraction, rich in hydrogen, light hydrocarbons and tar.
- A solid fraction, rich in carbon, called char.

The gases and vapours that first evolve from the solid are primary products. These vapours come directly from fragments of the carbonaceous structure, so there are many radical species. Once this fraction is in gas phase, these species may react among themselves, depending on the treatment temperature and residence time, to yield secondary (cracking) products. At medium temperatures (say 773 K), there are few secondary reactions, and the gas phase consists mainly of stabilized primary products. Consequently, the gas composition is highly dependent on the precursor used under mild conditions. As the temperature is increased, the secondary reactions become more important, yielding at extreme conditions (above 1273 K) methane, hydrogen and soot. If the temperature is 1073-1173 K, intermediates of soot formation (stabilized polyaromatics) can appear, together with olefins, methane, hydrogen, water and carbon oxides. If the heat treatment is carried out at high heating rates, cracking reactions are so quick that soot may be deposited over the char particles. A knowledge of what is happening, in terms of chemical reactions, during the carbonization is important for an understanding of the final properties of the final char.

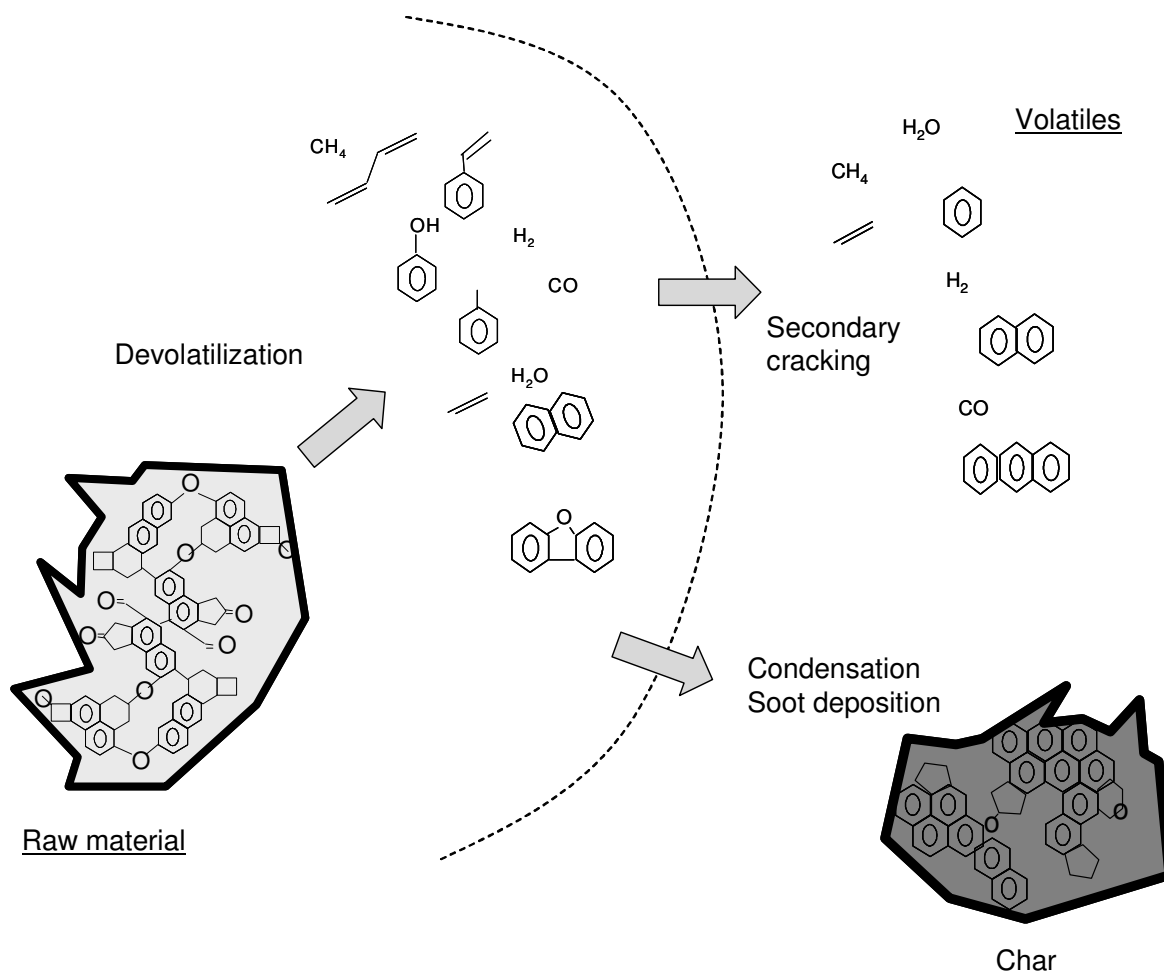


Fig. 10. Typical carbonization reaction scheme of a carbonaceous material

With respect to the solid char formed, there is an enrichment in both relative carbon content and aromaticity, compared to the precursor. Because a lot of mass is evolved during carbonization, this increase in aromaticity is accompanied by an increase in incipient microporosity, since a lot of functional groups and bridge chains are evolved, yielding void spaces. The char is composed of a group of disordered short graphitic crystals. Between the crystals there is little voidspace (the micropores), which are often not accessible from the external surface because the meso/macropore network is blocked by soot deposition (especially at high temperatures and high heating rate treatments). Thus, the carbonization heating rate is very important in establishing the final textural properties of the char. A high heating rate produces a very quick devolatilization, giving rise to a solid with a well developed meso and macropore network, a low density and a low abrasion and hardness index. On the other hand, low heating rate chars experience a slow release of volatiles during the devolatilization stage. This situation does not favour the formation of a large meso/macropore network, and consequently, both density and hardness values are higher than in the case of high heating rates. However, the incipient microporosity developed is as high as that created at the high heating rates. In consequence, a low heating rate treatment, at not very high

temperatures and long soaking times, seems to offer the appropriate conditions for producing chars that upon activation give rise to dense and hard activated carbons.

In industrial processes, it is common to use direct heated kilns in an oxidant atmosphere (steam with exhausted air from burners), at very low stoichiometric ratios. Final temperatures of 873 K and heating rates of 100-300 K h⁻¹ are reported [28].

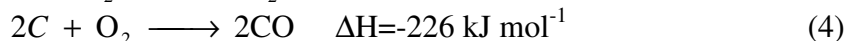
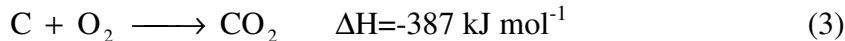
4.2.3. Activation

The product from the carbonization step has still only an incipient porous structure and cannot be used as an adsorbent unless this porous structure is enhanced, upgraded, or “*activated*”. The thermal activation consist in partially oxidizing the char with steam, carbon dioxide or air. These gases react with the carbon atoms and remove some of the mass of the internal surface of the solid, in the incipient micropores, creating a well developed microporous material. In addition, some internally blocked micropores may also become accessible due to tap burn-out.

The activation rate is conditioned by the characteristics of the precursor and the activating agent. The most reactive agent is oxygen, whereas the lowest reactive agent is carbon dioxide.

4.2.3.1. Activation with oxygen

Chemical reaction of carbon with oxygen yields simultaneously carbon monoxide and dioxide:



Both reactions are highly exothermic. Although the combustion reaction is one of the most important for mankind, the reaction mechanisms are still uncertain. It seems that both carbon monoxide and carbon dioxide are primary products, and the ratio CO/CO₂ increases with temperature. Due to the high enthalpy, the temperature of the reaction is extremely difficult to control, and often a reaction runaway (self ignition or uncontrolled temperature) takes place so that the reaction is governed by diffusion control burning the carbon only on the surface of the particle and not in the inner surface. Consequently oxygen activation is scarcely applied.

However, there is a typical process for producing a very specific developed microporous material using oxygen activation at laboratory scale. It consists of a cyclic process [29]: first oxygen is chemisorbed at low temperatures, below the ignition point (say 473-573 K); next the atmosphere is changed to inert, while at the same time the char is rapidly heated up to high temperatures. The initial chemisorbed oxygen burns out the corresponding carbon-oxygen complexes. After a short time, the sample is cooled down in an inert atmosphere. This method of producing activated carbon gives rise to extraordinary high capacity molecular sieves, and adsorbent materials with a narrow and defined pore size distribution. However, this is a very expensive process for carrying out at industrial scale.

4.2.3.2. Activation with steam

The steam gasification reaction also “burns out” carbon (like the combustion reaction) but follows an endothermic pattern.



This reaction has been extensively studied, not only for activating carbons, but also because it is the main reaction of water shift. Because this reaction is endothermic the reaction runaway does not take place. In addition to the heterogeneous reaction, gaseous products may react among themselves in gas phase, yielding:



Nevertheless, the kinetics of the two latter reactions is very low and they hardly take place.

From the kinetic point of view, the steam-carbon gasification reaction shows a typical reaction rate for most precursors, the conversion degree being expressed as:

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \quad (8)$$

where α is the carbon conversion degree (mass of reacted carbon vs. mass of initial carbon), K is the apparent kinetic constant (which depends on temperature and the partial pressures of the gas compounds) and n is the reaction order, which can have the following values [30]:

- $n = 0$. This is very unusual, although sometimes the reaction rate is independent of the carbon conversion degree in some catalyzed gasifications.
- $n = 1$. In this case, the reaction follows the uniform conversion model [31], which indicates that it proceeds under chemical reaction control, and the reactive agent first diffuses through the pore network and later reacts at any internal active site. The particle will retain its initial size during the conversion
- $n = 0.67$. This reaction order corresponds to the shrink core reaction model. The reaction is under diffusion control, and the oxidizing agent reacts only on the surface because it has no time to diffuse internally, so the particle size becomes smaller as the conversion degree increases. In this case, the apparent kinetic constant will depend on the particle size and parameters derived from internal diffusion, in addition to the parameters mentioned before.

In order to produce activated carbons, it is necessary that the steam gasification progresses under chemical control to allow internal porosity to develop inside the char particles. Otherwise the reaction would only take place on the outside of the particle. Due to the

specific nature of steam gasification, chemical control is achieved at relatively high temperatures. Consequently, steam can be considered as a good activating agent. In most situations, chemical control can be maintained at temperatures up to 1273 K. Internal porosity (in terms of the BET specific surface area or the micropore volume) increases with the conversion degree, although the micropore sizes also increase, which indicates that activation is taking place throughout the porosity. The way in which the internal porosity is developed (development of existing micropores by widening, which may even become mesopores at high conversion degrees) depends on what the active sites for the previously complex C(H₂O) are. The way in which porosity develops is similar for all chars but it is not exactly the same for several reasons. First, each char has a different origin and chemical structure, so the active sites are not the same. Second, most of the precursors have a mineral content, which is able to catalyse the steam gasification. This catalysis may affect slightly the way in which porosity develops. One example is the coconut shell char. Compared with other raw materials, coconut shells are excellent due to their extraordinary hardness and high and narrow micropore development. The reason for this behaviour is that the mineral matter of coconut shells contains appreciable amounts of potassium.

With regards to the apparent kinetic constant, there is experimental evidence that hydrogen inhibits the reaction kinetics significantly, whereas carbon monoxide does not. From this evidence, the apparent kinetic constant is an expression of the Langmuir-Hinshelwood type [32]:

$$K = \frac{k_1 \exp\left(-\frac{E_a}{RT}\right) P_{H_2O}}{1 + k_2 \exp\left(\frac{E_2}{RT}\right) P_{H_2O} + k_3 \exp\left(\frac{E_3}{RT}\right) P_{H_2}} \quad (9)$$

where k_i are Arrhenius type preexponential factors, E_a the activation energy, E_2 and E_3 adsorption enthalpies and P_i the partial pressures.

Steam activation is the most widely used method for producing activated carbons in the world. In terms of adsorption capacity, it easily reaches specific surface areas of 1000 m² g⁻¹ at 50% of activation conversion degree (regardless of carbonization yield), when an acceptable raw material with an initial ash content below 10% is used. Basically, steam activated carbons are microporous materials, with a micropore size that increases with the activation degree, but with no mesopore development. As an example, Figure 11 shows the nitrogen adsorption isotherms of activated carbon produced by the steam activation of an anthracite [33]. Each adsorption isotherm corresponds to an activated carbon with activation degrees of 20, 35, 50, 70 and 80% burn-off (samples: AC-720, AC-735, AC-750, AC-770 and AC-780 respectively), the sample AC-700 being the non-activated char. These isotherms not only provide specific numerical parameters correlated with adsorption capacity, but also provide certain qualitative information derived from their shape.

Thus, the char (non-activated) is at the base of the plot, with nearly no adsorption at all. For the rest of the samples, the sharp increase in adsorption at nearly nil relative pressures and the knee close to a horizontal plateau indicate a narrow microporosity (pores below 1 nm). As the knee becomes more open, the micropore structure changes from the narrow micropores to wide micropores. The occurrence of a positive slope of the plateau (in the relative pressure range of 0.2 to 0.7) is an indication that mesopore development has started. Thus, from Figure 11 it can be inferred that at low burn-off, the carbon has only narrow micropores. As the burn-off increases, the adsorption capacity clearly increases (the isotherm plateau has higher values) and the isotherm knee becomes more open, which is indicative of micropore development and an enlargement of the micropores. It should be noted that the knees start from the same point (close to the Y axis) for the last three samples, which is indicative of this enlargement. Only at very high burn-offs (80%) does this micropore widening lead to the partial formation of mesopores (positive slope). This tendency is valid for nearly any precursor with steam activation, with some differences regarding the starting material and kinetic conditions (e.g. the mesopore development could be higher at high temperatures).

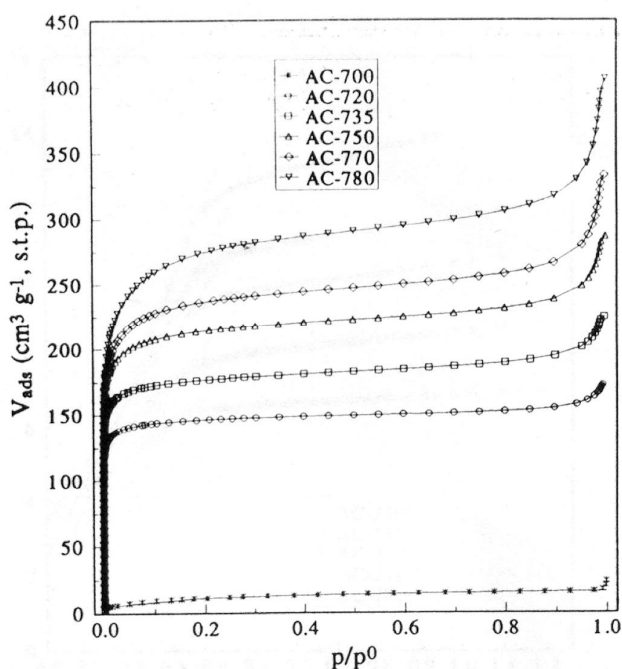


Fig. 11. Nitrogen adsorption isotherms for steam anthracite based carbons with different burn-off degrees [33]

4.2.3.3. Carbon dioxide activation

The heterogeneous reaction between carbon and carbon dioxide yields carbon monoxide:



following an endothermic pattern, which is positive for the activation process. The kinetic expression for the process is:

$$\frac{d\alpha}{dt} = \left(\frac{k_1 \exp\left(-\frac{E_a}{RT}\right) P_{CO_2}}{1 + k_2 \exp\left(\frac{E_2}{RT}\right) P_{CO} + k_3 \exp\left(\frac{E_3}{RT}\right) P_{CO_2}} \right) (1-\alpha)^n \quad (11)$$

where the meanings of all the parameters have been previously defined. The value of the reaction order n , as in the case of the steam gasification, may be: 0, 0.67 and 1 depending on the reaction control. From the kinetic point of view, carbon dioxide gasification is slower than steam gasification, for the same temperature and partial pressure.

Depending on the partial pressures of the reagents and products, the temperature where the transition takes place is around 1123 K (or even lower), when the reaction rate is not very high. Under chemical control, the porosity development attained is as high as that obtained with steam [34]. On the other hand, under diffusion control, porosity development is poor and unsatisfactory, giving rise to external particle burning [35,36]. Consequently, in order to work with carbon dioxide it is necessary to find out whether the process proceeds under chemical control or not. Usually, laboratory reactors with a low carbon dioxide mass flow vs. mass of carbon, operate under chemical control, whereas high carbon dioxide mass flow vs. mass of carbon (fluidized beds, rotary kilns, etc.) fall under diffusion control [37].

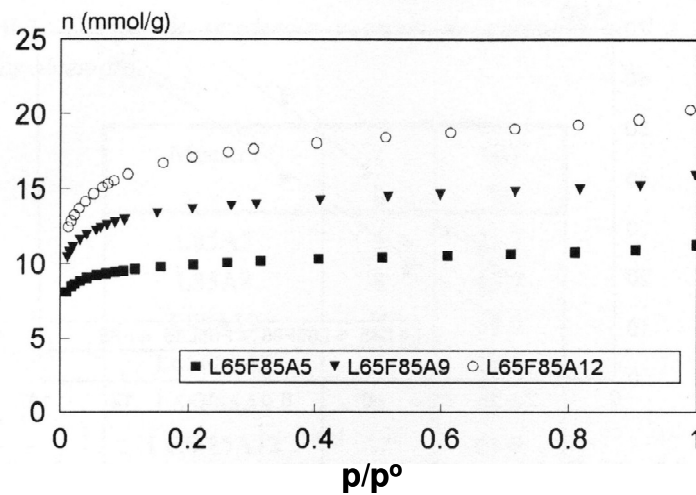


Fig. 12. Nitrogen adsorption isotherms of CO₂ activated carbons from a bituminous coal char, with activation burn-offs of 25, 48 and 62% [38]

An example of the variation of porosity development with the activation degree can be observed in Figure 12. This corresponds to the activation with CO₂ of a bituminous coal char at 25, 48 and 62% burn-off. Once again, it can be seen that a low activation degree gives rise to a narrow microporosity (close isotherm knee) and that higher burn-offs also produce

microporous materials. It must be noted that contrary to what occurred in the case of steam activation (Figure 11), the isotherm knees are less open (for all the samples) than those shown in Figure 11, and they separate from the Y axis at different heights.

4.2.3.4. Carbon dioxide vs. steam activation

Although industries have always used steam instead of carbon dioxide to produce activated carbons by thermal activation, there has been constant disagreement about which oxidizing agent performs better. It is clear that steam reacts under chemical control over a wide temperature range, thereby developing porosity. CO₂, on the other hand, may react under undesirable diffusion control, which represents an obstacle for its use as an oxidizing agent. The porosity developed (assuming chemical control for both agents) from these reactive gases is compared in Figure 13. The Figure shows two activated carbons, with similar burn-offs, from the same starting material, one activated with steam and the other with CO₂ [39]. It is clear that both samples attained similar adsorption capacities (similar isotherm heights). However, the porosity developed by CO₂ is a little narrower than that of the carbon activated with steam (slightly more open knee for the latter, with some positive slope in the plateau). The choice of which carbon to use will depend on the final application. Thus, carbons with narrow or normal micropore sizes are usually more appropriate for gas adsorption, whereas carbons with an open micropore structure are preferred for liquid phase adsorption, since the wide micropores facilitate diffusion of the solute into the particles.

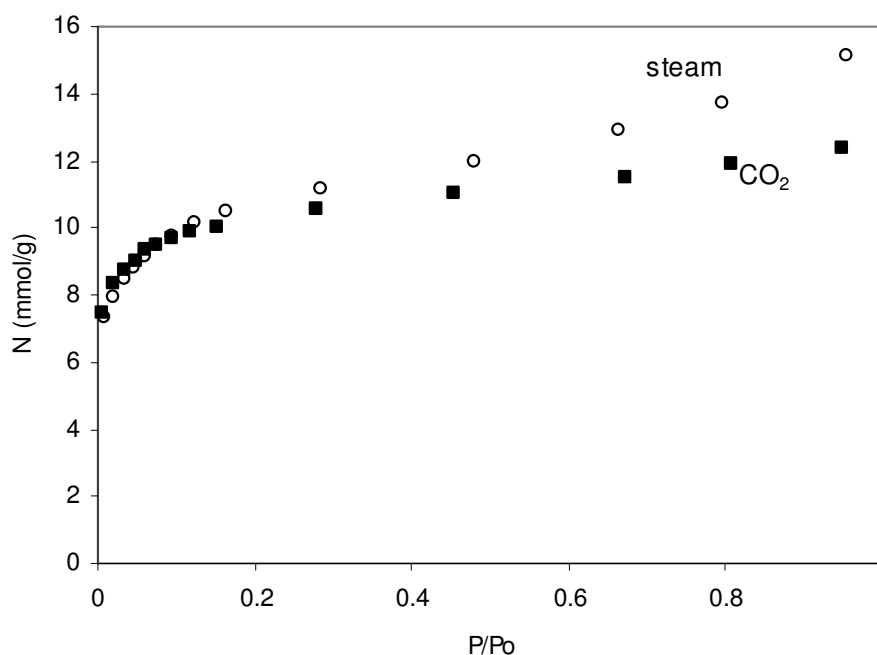


Fig. 13. Nitrogen adsorption isotherms of steam and CO₂ activated carbons at similar burn-offs [32]

Figure 14 shows the variation in the pore diameter with the pore size distribution at different activation degrees for these two activating agents, for the activation of a bituminous

coal char in a fixed bed reactor [39]. The carbons activated with CO₂ present a micropore structure of the same pore size regardless of burn-off. Only the adsorption capacity is improved when the burn-off increases. This means that new micropores, of similar sizes to the existing ones, were developed. On the other hand, the carbons activated with steam present a pore widening which increases with the burn-off. Thus, the mean micropore size increases with burn-off enhancing, its adsorption capacity due to the enlargement of the existing pores and the destruction of the initial narrow micropores. In a comparison of the micropore size distribution at 1 nm, it can be observed that the carbon with the higher degree of activation has practically no pores of this size with respect to the less activated carbons. This does not mean that CO₂ activated carbons are better for adsorption applications than the steam activated carbons. Micropores are necessary since they are the sites responsible for adsorption. However, some applications will require only narrow micropores while others (specially liquid applications) will require wide micropores.

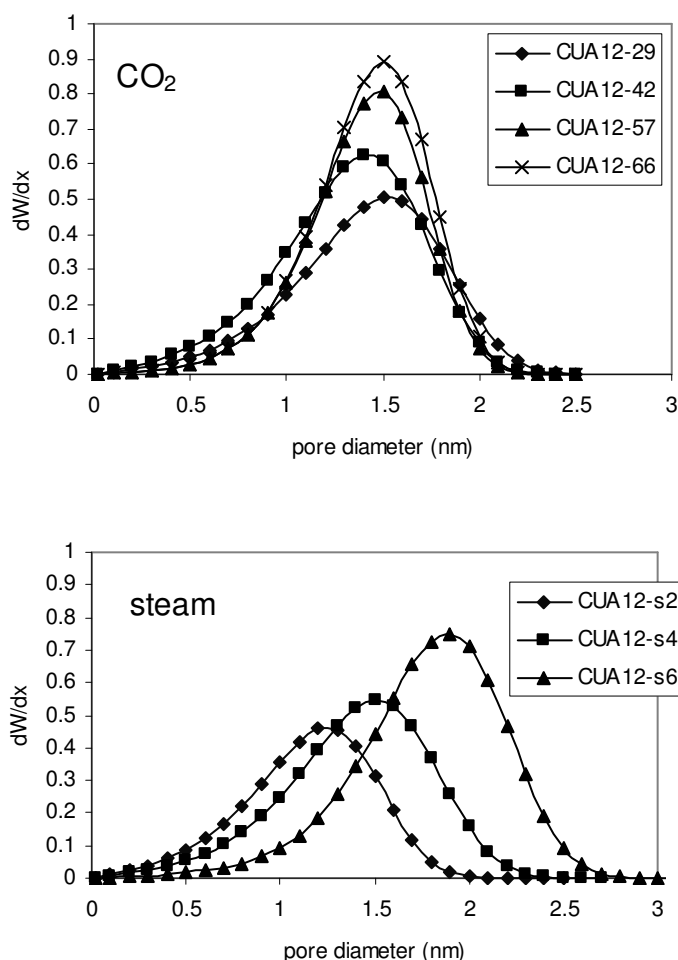


Fig. 14. Micropore size distribution of CO₂ and steam carbons at different burn-offs [39]

Although the tendency explained is valid in relative terms for any raw material, each specific raw material must be studied individually, as the quantitative parameters cannot be predicted due to the influence of the organic structure of the precursor and the different behaviours of the mineral contents of each precursor.

4.3. Chemical Activation

A second commercial route for producing activated carbons involves the reaction of a carbon precursor with a chemical reagent, and is known as chemical activation. Porosity develops at the same time as the transformations that occur during heat treatment in an inert atmosphere at temperatures in the range of 623 to 1173 K. Compared to the two kilns that are normally employed for carbonization and activation in industrial thermal activation, chemical activation only requires a single kiln. The reagents that have been most used by industry are zinc chloride, phosphoric acid and potassium hydroxide. Each reagent produces a very different pore development in the carbon precursor. The feasibility of chemical activation processes is strongly dependent upon efficiently recovering the reagent for recycling. This involves a subsequent leaching stage, followed by an additional operation consisting of drying the washed carbon.

This section will describe the chemical activation process with the most commonly used reagents: zinc chloride, phosphoric acid and potassium hydroxide. Other low-volume processes utilize various Lewis acids such as aluminium chloride and ferric chloride with fibrous materials such as rayon (a product of cellulose) to produce activated cloths or fibres.

4.3.1. Zinc Chloride Activation

The zinc chloride process was the principal method of chemical activation up to 1970, and it is still used in China. The preferred precursors are those with a high amount of volatiles (and oxygen content) such as lignocellulosic materials. Wood, therefore, is the most common precursor, although other materials, such as ground olive stones, are also used. Low recovery efficiencies, corrosion problems, the presence of residual zinc in the carbon, and the need for stringent control of plant emissions have contributed to their displacement by phosphoric acid.

Initially, the precursor is mixed with the chemical in an aqueous solution to form a paste, which is later evaporated. During evaporation, there is a weakening of the lignocellulosic structure due to hydrolysis reactions (with loss of volatile matter), leading to an increase in elasticity and a swelling of the precursor particles [40]. The higher the amount of zinc chloride, the stronger the changes during impregnation and evaporation. After evaporation, the impregnated carbon is heat treated in an inert atmosphere at final temperatures between 773 and 1073 K. The $ZnCl_2$ restricts tar formation, preventing the contraction of the particle and giving rise to a wide and open microporosity (border micro-mesopores). This results in a slightly higher adsorption capacity and a wider porosity than in the case of thermal activation. Figure 15 shows the nitrogen adsorption isotherms of activated carbons obtained using different $ZnCl_2$ /precursor ratios.

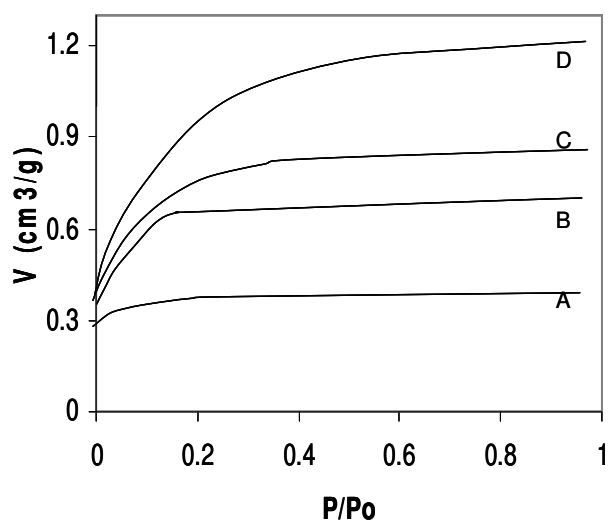


Fig. 15. Butane adsorption isotherms of ZnCl_2 based activated carbons with heat treatment temperature at 773 K and Zn/precursors ratios of (A) 0.24, (B) 0.48 and (D) 0.96. (C) was made at HTT of 1073 K and Zn/C of 0.96 [40]

It can be seen that all the isotherm knees leave the Y axis at the same level, although each one reaches a different plateau level. However, the knees are so open that the plateau is not reached above relative pressures of 0.4, which means that the porosity developed is wider than that obtained with thermal activation. The carbon yield is much higher than that achieved with thermal activation but the particle density and abrasion/hardness values are lower.

4.3.2. Phosphoric acid activation.

The ability to produce high surface area carbons with phosphoric acid in an inert atmosphere depends primarily on the structure of the starting material, the acid-to-precursor ratio and the heat treatment conditions (time-temperature profile and maximum heat treatment temperature). As with ZnCl_2 activation, wood and some agricultural by-products (such as almond shells and olive stones) as well as carbonaceous materials with a high volatile content are the precursors most commonly used in this method of activation.

The steps involved in the production of activated carbons by chemical activation with H_3PO_4 are:

- 1) grinding and classification of the starting material;
- 2) mixing with phosphoric acid (recycled acid plus make-up);
- 3) heat treatment initially at a temperature between 373 to 473 K in an inert atmosphere.
- 4) continuing the heat treatment at a final temperature between 673 to 773 K;
- 5) washing the product to recover acid for recycling, followed by drying and classification of the washed carbon.

Both steps 3 and 4, can be carried out in the same kiln/reactor and no cooling down is necessary between steps. Soaking times at these two temperatures are around 1 hour for each. Compared with carbons produced by thermal activation, the wood-based carbons activated

with H_3PO_4 have a lower density, lower abrasion resistance and a more developed mesoporosity. These properties are related to the hollow fibrous structure of wood, which gives rise to an important macropore volume in the activated carbons.

Frank Derbyshire and coworkers at the University of Kentucky [7,41] who carried out an extensive study of the H_3PO_4 activation of different raw materials, proposed an activation mechanism for the activation of lignocellulosic materials, the only materials which display interesting adsorption characteristics with this chemical reagent. Wood or lignocellulosic materials (hard fruit stones and shells) are composed of cellulose (42-50%), hemicellulose (19-25%) and lignin (16-25%). Wood is often compared to a composite material, where most of the cellulose forms microfibrils with a crystallite structure, whereas hemicellulose and lignin form the matrix, an amorphous paste that surrounds the microfibrils.

A H_3PO_4 /precursor ratio of 1.5 is the most frequently used proportion in this method of activation. After the chemical reagent is mixed with the precursor, the mixture is slowly heated up to 373-473 K (low temperature treatment). During this stage, the acid attacks the hemicellulose and lignin hydrolyzing the glycosidic linkage to produce polysaccharides (hemicellulose) and cleaving the aryl ether bonds of the lignin [42]. These reactions may be accompanied by secondary reactions such as degradation and condensation. During this low temperature treatment, there is an extensive evolution of CO/CO_2 and methane (which would not occur under this heat treatment without H_3PO_4). This process also leads to a reduction in the volume of the particles.

When the temperature is increased, during the second heat treatment, towards the final temperature, the rate of weight loss diminishes appreciably and the structure begins to dilate, developing porosity. Under this regime, crosslinking reactions promoted by phosphate esters among the cellulose fibres are predominant. These produce the effect of dilation, which is maximum at around 473-523 K. Figure 16 shows the porosity developed in terms of surface area vs. the heat treatment temperature and Figure 17 shows the particle dimensions vs. the heat treatment temperature for an oak wood precursor, together with the variation undergone when only thermal pyrolysis is applied.

It can be observed (Figure 16) that micropore development begins a little above 473 K, increasing sharply and attaining a maximum at around 573 K, with a BET surface area of $1500 \text{ m}^2 \text{ g}^{-1}$. This micropore increase runs parallel to particle dilation (Figure 17). The particles undergo an initial contraction, which is then followed by a dilation above 473 K. Mesopore surface area also reaches a maximum at 723 K. As a consequence, the micropores widen into mesopores when the material is heated from 573 to 723 K. After 723 K, the micro and mesopore areas experience a decrease, which is accompanied by a contraction of the particles. These changes are accompanied by a shrinkage of the pore size distribution. The reason for this contraction is the breakage of the (previously formed) phosphate crosslinkages between the cellulose fibres. This leads to an increase in the aromaticity of the solid resulting from a thorough reorganization of the structure of the solid.

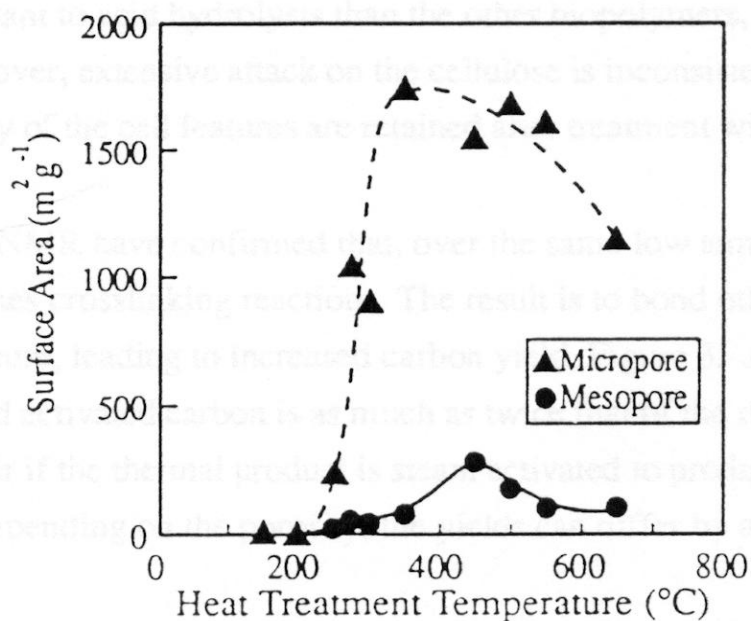


Fig. 16. Micropore and mesopore surface area vs. heat treatment temperature in the H₃PO₄ activation of white oak [41]

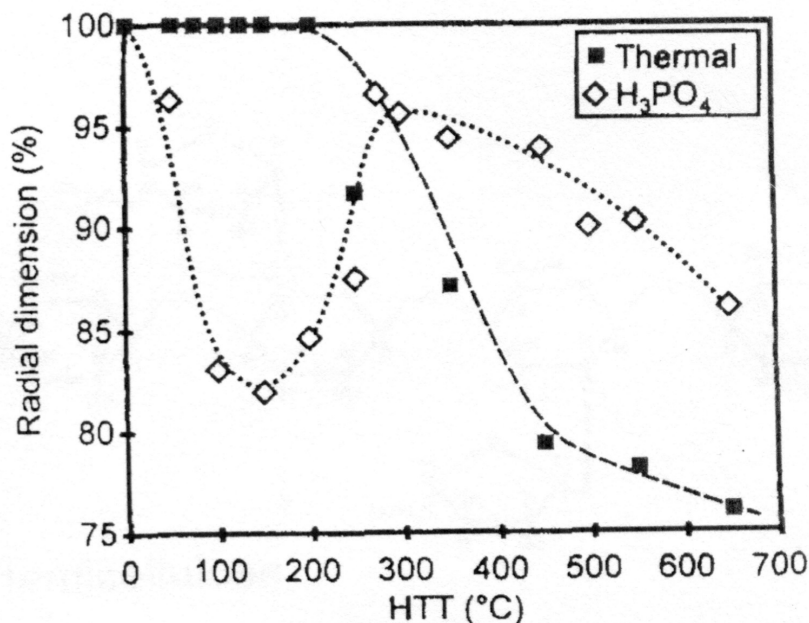


Fig. 17. Particle size vs. heat treatment temperature in the H₃PO₄ activation of white oak [42]

Regarding the influence of the gas atmosphere during the heat treatment, it has been reported [43-44] that the use of nitrogen gives the best results for porosity and carbon yield. The use of air also gives good results in terms of porosity but a much lower yield. CO₂ or steam result in activated carbons with a lower adsorption capacity (i.e. lower porosity). However, it must also be pointed out that the phosphorous content of the resulting activated

carbons was much lower when the atmosphere employed was air or steam (ca. 1%) and not nitrogen (ca. 4.5%).

Summarizing, the phosphoric acid activation of lignocellulosic materials requires two consecutive heat treatments, at a low heating rate, the first at around 423-473 K, and the second at 673-773 K, to yield an activated carbon with over $1500 \text{ m}^2 \text{ g}^{-1}$ with a wide open porosity. The yield of activated carbon during phosphoric activation (around 50%) is also an interesting factor to be considered since this is higher than the yield obtained by only pyrolyzing the starting material. Figure 18 shows the nitrogen adsorption isotherm of a typical commercial H_3PO_4 activated carbon, NORIT CNR115 (manufactured by NORIT UK, Glasgow), based on olive stones, which has a BET surface area of $1700 \text{ m}^2 \text{ g}^{-1}$. The shape of the isotherm is similar to that of ZnCl_2 and shows a wide open micropore structure. The Y axis values and the form of the isotherm can be compared with those of Figure 13 (thermal activation) which exhibits a much more microporous carbon with a lower adsorption capacity under thermal activation. The other isotherm corresponds to the CNR115 heat treated at 1173 K. There is a clear reduction in adsorption capacity, due to the contraction brought about by the carbonization of this dilated material [45].

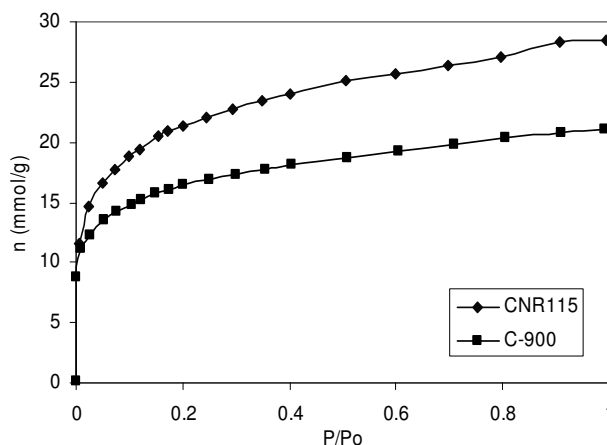


Fig. 18. Nitrogen adsorption isotherms of commercial NORIT CNR115 and its carbonized material at 1173 K [45]

Figure 19 shows the adsorption capacity attained with other precursors such as a bituminous and a subbituminous coal, vs. the heat treatment temperature and compared with wood [46]. It is clear that phosphoric acid activation must only be applied to lignocellulosic materials since the coals hardly develop any porosity.

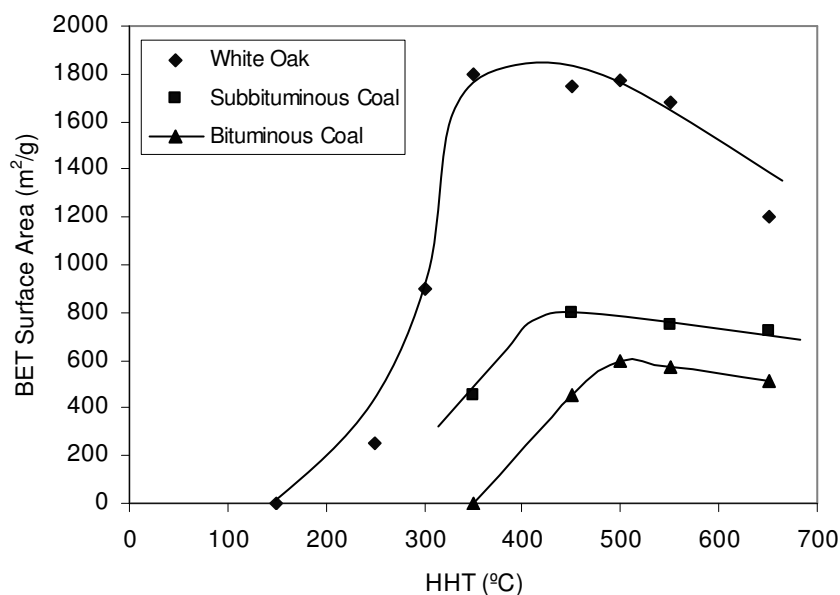


Fig. 19. Specific surface area developed with coal based H_3PO_4 activated carbons, vs. final heat treatment temperature, compared to White Oak based carbons [46]

4.3.3. Potassium Hydroxide Activation

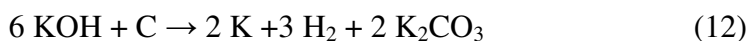
In the 1970s, researchers from the AMOCO Corporation, USA, [47] developed a process that produced extremely high surface area carbons (super activated carbons, with over $3000 \text{ m}^2 \text{ g}^{-1}$) by chemical activation with alkaline hydroxides, especially KOH. It was commercialized by the Anderson Development Company in the 1980s, and was subsequently licensed and operated at pilot scale by Kansai Coke and Chemicals Ltd, Japan, manufacturer of MAXSORB. This is a completely different process, with a different chemistry with respect to the previously described $ZnCl_2$ and H_3PO_4 chemical activation.

Unlike other chemical activation processes, the most appropriate raw materials are those with a low volatile content and a rich carbon content such as high rank coals, previously devolatilized chars or petroleum coke. Thus, most of the examples cited in the work of Wennerberg and O'Grady [47] referred to petroleum coke as a raw material.

In this activation process, KOH is mixed with the precursor, either by impregnation with aqueous solution or just physically. The precursor can be either in powder or granular form. The KOH/precursor weight ratio normally ranges between 2 and 4. As occurred in the case of H_3PO_4 activation, this activation method usually requires two consecutive heat treatments in an inert atmosphere; the first one at low temperature (but above 373 K) and the second at 973-1173 K. The first treatment is used merely to impregnate the precursor surface with KOH by evaporation of the water solvent if the impregnation method is used. Otherwise, the first heat treatment temperature is not necessary. However, when using brown coals as raw materials, there is significant interaction between the KOH and the precursor during the drying step [48].

In the second heat treatment, the temperature is higher than that required for H₃PO₄ activation, and similar to the temperatures used in the case of thermal activation. The treatment requires a soaking time of approximately one hour at maximum temperature. After carbonization, the product is washed with water (or HCl and water) to remove any soluble salts and to recover the carbon. The latter step also removes some of the original mineral matter contained in the raw material.

As mentioned above, the way in which the KOH acts is very different to that of the other activation reagents. In this case, KOH reacts with the carbon skeleton, producing solid and gaseous products. At the same time a carbon burn-off occurs giving rise to porosity. Experimental evidence shows that hydrogen and metallic potassium are formed during the reaction, as well as CO and CO₂ (which come from the carbon skeleton) and potassium oxide. Lillo-Ródenas and coworkers [49] proposed that the chemical reaction involved is:



where the potassium carbonate decomposes further to form K₂O and CO₂. This reaction is thermodynamically possible (in terms of the Gibbs free energy) above 873 K, and it agrees with all the experimental evidence.

In general, the higher the KOH/precursor ratio, the stronger the changes produced and the higher the adsorption capacity. The final temperature of the treatment may have a certain influence on the adsorption capacity developed, but much less than the KOH/precursor ratio. Basically, KOH activation produces high adsorption capacity carbons of extremely narrow microporosity and with no mesopores at all. Specific surface areas of more than 1500 m² g⁻¹ can be attained with just medium KOH/precursor ratios. When the KOH/precursor ratio is increased more porosity is developed (over 3000 m² g⁻¹). However, the micropore size distribution is widened to include pores ranging from large size micropores to small size mesopores, although it is not possible to talk of fully formed mesopores. Figure 20 shows the adsorption isotherms of an anthracite activated with KOH at 973 K, with KOH/anthracite ratios ranging from 1 to 5 [50]. In the figure nomenclature, the number after the K denotes the KOH/anthracite ratio. It can be seen that a ratio of 1 gives an extremely narrow microporous carbon of medium adsorption capacity (726 m² g⁻¹), with a flat isotherm and a knee with almost no angle. A KOH ratio of 2 also yields a narrow microporous carbon, but with a very high surface area (2021 m² g⁻¹). At this point, the higher the KOH ratio, the higher the surface area and the isotherm plateau level, but the isotherm knee also becomes wider as the KOH ratio increases. It should be pointed out that in the relative pressure range between 0 and 0.2, the adsorption capacity of the sample with a KOH ratio of 4 is higher than that of the sample with a KOH ratio of 5. However, at higher relative pressures the opposite is the case. This is indicative of the micropores widening to become mesopores due to an excess of KOH.

The gas regime in the reactor where carbonization takes place has a strong influence on the properties of the resulting carbon. A high carrier gas flow results in the development of micropores. This is especially the case at low temperatures (ca., 973 K) and low

KOH/precursor ratios, due to the dilution of the reaction products, which favours the chemical reaction [50].

As mentioned above, KOH activation is usually carried out in an inert atmosphere. Air cannot be used since this would burn up the precursor and it would react with the metallic potassium formed. In a steam atmosphere the porosity developed is much lower than that formed with nitrogen, although the carbon it is still of good quality. On the other hand, an atmosphere of carbon dioxide produces a carbon with no porosity at all [26], even if the process is carried out at the final temperature when the gasification of the uncatalyzed carbon dioxide takes place.

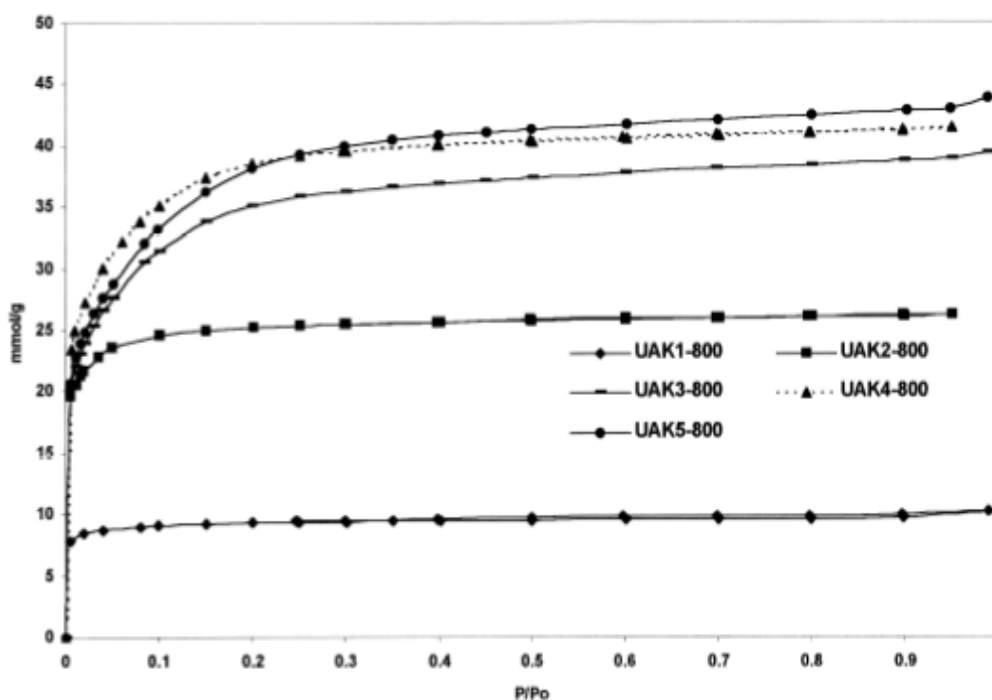


Fig. 20. Nitrogen adsorption isotherms of carbons at different KOH/C ratios [50]

4.4. Different Types of Carbon Adsorbents

In previous sections, it was explained how different precursors can be used to produce activated carbons and the type of porosity developed depending on the type of activation method applied. Thus, thermal activation normally yields adsorbents with a medium to high adsorption capacity, a medium micropore size distribution and no mesopore formation (except in the case of high burn-off ratios, where micropores may be of a large size). Phosphoric acid activation yields a carbon with a higher adsorption capacity than thermal activation and a wider micropore size distribution (even in the low mesopore range), whereas KOH yields extremely narrow microporous carbons.

These characteristics, however, cannot be used to say which raw material or which activation method produces the best carbons in absolute terms. In fact, each type of carbon is

suiting to a particular application. In addition, the economic aspects of the process (including the cost of the raw material) also play an important role in the selection of the most suitable carbon for a specific application.

Other properties of activated carbons, however, may be even more important than their textural properties. One example is particle size. A classification of carbon adsorbents based on size divides them into Powdered Activated Carbons (PAC) or Granular Activated Carbons (GAC). For certain specific applications a choice must be made between PAC or GAC regardless of porous properties. For example, in order to clean up a gas stream in a fixed bed, a granular material must be used. Otherwise the pressure drop would be enormous. Furthermore, granular carbon must be dense, hard and with a low abrasion index.

This section deals with the most relevant aspects of the different types of activated carbon including shapes other than PAC and GAC such as activated carbon fibres and other special forms of carbon (see Figure 21).

4.4.1. Powdered Activated Carbon

Powdered Activated Carbon, or PAC, has a typical particle size of less than $100 \cdot 10^{-6}$ m, the most common values being around $15\text{--}25 \cdot 10^{-6}$ m. About 50% of the total production of activated carbons is PAC. Normally this is used in applications where the solute may have problems in diffusing from the transport pores to the adsorption pores and where an enormous amount of time would be required to reach equilibrium if a granular form were used.

In liquid phase applications batch stirred vessels are often used for treatment with PAC. The type of carbon, contact time and amount of carbon depend on the degree of purification required. The efficiency of the treatment may be improved by applying a continuous counter-current of carbon suspension flow in multiple stages. The carbon is later separated from the liquid by settling or filtration. Filter aids such as diatomaceous earth are sometimes used to improve the process. In gas applications, PAC is normally added to a high speed gas stream. It is pneumatically transported, and then filtered by plate and frame equipments or by electrostatic precipitators. Typical applications for PAC are industrial and municipal waste water treatments, sugar decolorisation, the food industry, pharmaceutical uses, and mercury and dioxin removal from a flue gas stream.

In the case of PAC based on thermal activation, the initial raw material, whether briquetted or non-briquetted, is first crushed and milled to the appropriate particle size prior to the carbonization and activation stages. Nevertheless, the resulting particle size is not the final size of the powdered activated carbon. The particle size of the raw material is normally coarser (with a wide particle size distribution ranging from fines to quite large particles) than that of the PAC. During the carbonization and activation stages, the material suffers attrition, and the particle size distribution may change considerably. After activation, the material is screened and divided into different granular sizes (frequently called broken GAC) and powder sizes. After the screening the fraction composed of the broken GAC, which has no market application (between 100 and $1000 \cdot 10^{-6}$ m), is usually pulverized to PAC, which is then added to the powdered fraction. Because it is difficult to control a continuous high

temperature process with a powdered material, the particle size reduction to powder is carried out after the activation process is completed.

However, chemical activation usually produces a powdered material, even if it is applied to a granular material. In any case, the reagent impregnation efficiency is better with small (but granular) particle sizes than with large ones. This point is of special significance in KOH activation, where the reduction of the particle size and powder generation is very important, and where the higher the KOH/precursor ratio the smaller the particle size.

Another point that deserves consideration is the fact that PAC is not a particularly well developed carbon adsorbent. This is because some of the characteristics that are important for other forms of carbon adsorbents such as high density, hardness and abrasion index are irrelevant in the case of PAC. In addition, PAC must be discarded after use and cannot be reused. This implies that the cost of producing PAC must be kept to a minimum. At present, investment in R&D for the development of better PAC adsorbents is negligible, most of the industrial research focuses on the GAC and the special forms of carbon adsorbents.

4.4.2. *Granular Activated Carbon*

Granular Activated Carbon, or GAC has a mean particle size between 1-5 mm. It is usually used in fixed bed adsorbers in continuous processes and with low pressure drops, in both liquid and gas phase applications. Most of the gas phase applications (gas purification, solvent recovery, air filtering and gas masks, gas separation by PSA, catalysis, etc.) use GAC. In addition, GAC is displacing PAC in many liquid phase applications such as gold extraction and drinking water treatment. GAC has the advantage, compared to PAC, of offering a lower pressure drop along with the fact that it can be regenerated or reactivated and therefore reused more than once. However, GAC must have, in addition to the proper micropore size distribution, a high apparent density, a high hardness and a low abrasion index. To meet these requirements a lot of R&D is focused on the development of better GAC.

Granular activated carbons can be divided in two groups:

- Unshaped or broken GAC
- Shaped GAC of a specific form

Shaped GAC is a carbon, which has been processed to have an specific shape such as that of a cylinder. These cylinders are obtained either by pelletisation or by extrusion of powder carbon and binders. Broken GAC, on the other hand, is the name given to irregularly shaped particles, which have merely been crushed and screened. Due to the fact that the size of briquettes formed from PAC and binders is normally very large, these briquettes must be crushed and milled again, as a result of which they acquire a broken shape. In consequence, briquetted activated carbons belong to the broken GAC group.

There are several reasons for the production of shaped GAC. These differ depending on the activation production method employed. Thus, in the case of the thermal activation (mainly steam activation), one of the reasons is to ensure that the particle has a relatively high internal porosity. This facilitates the diffusion of the activating gas and ensures a homogeneous activation throughout the whole particle. Another important point is that shaped

carbons have a higher density and hardness and a lower abrasion index than broken GAC. Most cylindrical shaped GAC produced by steam activation are based on extrusion, and are frequently called activated carbon extrudates.



Fig. 21. Different forms of carbon adsorbents

The production of activated carbon extrudates by steam activation does not follow the general scheme of Figure 8. In this case, after crushing the raw material is first devolatilized at high temperature and then finely pulverized, resulting in a powdered char. The powdered char is then mixed with appropriate binders to form a paste with lubricant properties, which is extruded. Normally several binders are used to form the paste because they each have different tasks: a) to provide lubricant properties to allow the extrusion of the paste b) to transform the wet extrudates into hard and consistent short cylinders during the drying step (low temperature binder), and c) to act as a high temperature binder in the activation step. The type and composition of the binder is a matter for further research, since the final hardness and abrasion index is dependent on the binders. Consequently, it is not unusual for them to be a mixture of three binders, each with a specific mission.

Pitch is a common high temperature binder. The extrudates with green pitch are preoxidized at medium temperatures in order to stabilize the pitch. Crosslinkages are created through the graphene layers in order to transform the fluid state into a solid skeleton in a subsequent high temperature treatment, and prevent the complete pyrolysis of the pitch. This step is similar to the stabilization of carbon fibres, after the melt spinning step [51].

After stabilization of the extrudate, the next step is regular steam activation at high temperature in order to develop porosity throughout both the char powder and the stabilized-carbonized pitch. The procedure must be performed in this order, otherwise the binders would block the entire pore network.

In the case of chemical activation, the reasons for processing the shaped GAC is that the direct kiln product is dusty and covered with a lot of powder, even when a granular material is fed in. In addition, chemical reagent dispersion is better when starting with low particle sizes. For phosphoric acid activation, there is a special method for pelletizing a lignocellulosic flour with phosphoric acid (which has lubricant properties). After this treatment the pellets are heat treated using the normal activation process [52]. However, the quality attained, in terms of density, hardness and abrasion index, with phosphoric acid activation is worse than that of the steam extrudates. In the case of KOH activation, the product obtained is nearly always in powder form (especially at high KOH vs. carbon ratios), or at least, it has a high attrition level. In consequence, the cylindrical shape must be sought after the activation step. Otherwise the shape would be lost during activation. The use of binders in briquetization/pelletisation/extrusion with a material that is already activated implies a large loss of adsorption capacity by pore blockage [53]. Consequently, there is widespread interest in developing a KOH based GAC which has the same adsorption capacity as the KOH based PAC.

4.4.3. Other forms of carbon adsorbents

Although activated carbon is considered to be a satisfactory general adsorbent, the new applications demanded by advancing industrial technology require more and more sophisticated materials.

4.4.3.1. carbon fibres

Activated carbon fibres (ACF) are, basically, carbonized carbon fibres which are subsequently heat treated in an oxidizing atmosphere, i.e. activation step. ACF began to be developed in 1970, together with activated carbon fabrics [54]. Interest was then focused on developing activated fabrics, and as the precursor was viscose rayon, single viscose activated fibres were produced. Viscose rayon is a fibre shaped material composed mainly of cellulose and it decomposes when heat treated directly, without melting. Rayon is used mainly in the textile sector, where the above mentioned fabrics and fibres were produced. Later, other precursors for ACF were used such as saran and phenolic resins [55], which are thermoset polymer materials. Thermoset polymers first melt at relatively low temperatures, and the liquid paste is spun through a fine nozzle to produce fibres, as it cools. When the spun fibres are heat treated again, they decompose directly without passing through a liquid phase, yielding an isotropic carbon fibre which can subsequently be steam activated.

At the beginning of the 1980s, interest became focused on developing ACF by the steam activation of conventional carbon fibres (CF), a fibril material whose main application was to reinforce polymer matrix composites. Poly-acrylo-nitril (PAN) based ACF was first produced by Toho Rayon Co. (Japan). At the end of the 1980s, interest centred on developing ACF from inexpensive precursors such as pitch based carbon fibres.

In summary, activated carbon fibres are produced, mainly, by the thermal activation of carbonized (and of course stabilized) carbon fibres. These carbon fibres may have been manufactured for purposes other than as an ACF precursor (like PAN based CF, mesophase pitch based CF) or specifically as a ACF precursor. For most CF precursors, the fibres are produced from direct melt spinning, resulting in the so-called "green" carbon fibres. These are later stabilized by a preoxidation process with air, and finally carbonized at high temperatures [14].

As in the case of common activated carbon, a good ACF precursor must be non-graphitic and non-graphitizable CF, isotropic in nature. CF with excellent properties for mechanical composite reinforcement, such as PAN and mesophase pitch based CF present highly oriented graphitic structures, which are anisotropic in nature and have no incipient porosity (Figure 221 a) [56]. When these CF are steam activated, the oxidizing agent does not react by developing porosity due to the fact that the atomic structure is ordered and gasification eliminates the graphite planes. In the case of isotropic carbon fibres, from either a thermoset material or an isotropic pitch, the aromatic planes are not oriented (Figure 22 b), and so the oxidizing agent during the activation process is able to develop pores among the disordered structure. As an example, the steam activation of PAN based carbon scarcely reaches $700 \text{ m}^2 \text{ g}^{-1}$, even at a high burn off, whereas the steam activation of coal pitch based CF easily attains $1500 \text{ m}^2 \text{ g}^{-1}$ at 50% burn-off, which represents a 50% higher adsorption capacity than a steam activated carbon [57].



Fig. 22. Scheme of the fibre cross section of (a) an anisotropic (PAN type) CF and (b) an isotropic (pitch type) CF

As a rule, ACF not only presents a higher adsorption capacity than conventional GAC, but the pore network is also different due to the fibril structure, which ensures a much higher adsorption kinetics. The reason is that in GAC, the adsorbate must diffuse throughout the macro and mesopores before reaching the micropore or adsorption sites, whereas the micropores are directly accessible from the external surface in the ACF (Figure 23). Consequently, there is no resistance to the diffusion of adsorbates through to the adsorption pores because there is no meso/macropore network.

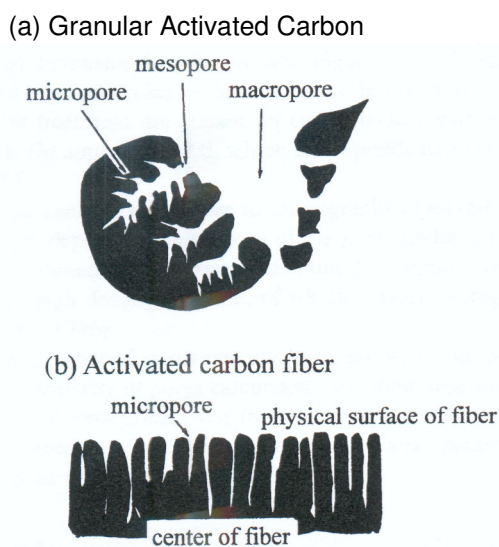


Fig. 23. General scheme of the micropore location in (a) GAC and (b) ACF

4.4.3.2. Carbon fabrics and felts

To meet the engineering requirements of specific applications such as adsorption, gas separation, catalyst supports, etc. activated carbons can be manufactured in the form of fabric or felt in order to benefit from their low pressure drop, high contact efficiency, flexibility and high adsorption capacity. They can also be manufactured from different synthetic cloths like rayon, kevlar, aramid, etc. Both thermal (carbonisation followed by gasification) and chemical activation (heat treatment after impregnation of the cloth with a Lewis acid solution) are used to manufacture these particular forms of activated carbon. Because of the inherently

greater surface area available on woven or otherwise fixed fine fibers, compared to packed powder or granular forms of a substance, the fabric form can be made to develop a greater effective surface area for adsorption. When the cloth fibers are highly activated, they may display as much as two to three times the surface area of activated granules. Furthermore, the fabric is typically lighter in weight, can be arranged in many different stable configurations, and is easier to maintain or replace.

4.4.3.3. *Monolithic structures*

The next generation of adsorption processes for environmental use are likely to be based on monolithic adsorbents. These have the potential to overcome many of the limitations of the conventional granular beds in terms of substantially reduced pressure drop, enhanced regenerability and elimination of dusting and attrition. These benefits may lead to substantial reductions in both capital cost and energy consumption along with improved operability. The use of monolithic systems will also permit the development of regenerable systems rather than single use and disposal ones. Solid monoliths are used in applications such as gas storage and gas separation, in order to reduce interparticle spaces and to optimise the adsorption capacity (volume per volume) of the activated carbon. In some applications such as catalyst supports or adsorption, the monoliths must have fine parallel channels through which the gas or liquid can circulate.

Two different types of monolithic structures are to be distinguished: coated monoliths and integral monoliths. The former consist of a monolithic backbone and a support layer that is coated onto or in the structure. The monolithic structure, which is either a ceramic or metallic monolith, supplies the mechanical and geometrical properties, whereas the support layer provides the adsorptive and/or catalytic properties. The second type, the integral structure, is made entirely of support material which must provide the mechanical, geometric and adsorptive properties by itself.

Carbon-based monolithic structures are only occasionally a topic in scientific literature. However, there are several patents that describe a variety of preparation procedures for these materials [58].

Three different methods for preparing carbon-coated monoliths have been reported.

- 1) "The melting method" consists in heating a ceramic structure together with a coal tar pitch in an inert atmosphere. Upon heating the pitch melts and penetrates the pores of the ceramic structure. The composite is then, heated up to 1070-1273 K in order to carbonize the pitch.
- 2) In the "dip-coating" method a ceramic structure is dip-coated into a liquid polymer or polymer solution (e.g. poly furfural alcohol or resins, furan-type resins) by immersion in the liquid polymer until the structure is completely soaked. The excess polymer is then removed by air, vacuum, or some other method, and the polymer is allowed to solidify. Finally the polymer is converted into a carbon by heating the composite up to 873-1273 K.

- 3) The “chemical vapour deposition” method is based on the chemical vapour deposition of a carbon layer on top of a ceramic support.

Integral-type monolithic structures are produced by extrusion. The extrusion mixture generally includes the following components: a type of carbon or carbon precursor such as activated carbon particles, graphite, carbon fibres, etc., a binder such as phenol resin, hydroxylcellulose, coal tar pitch etc. and extrusion aids/plasticizers such as water or polymers. Typical preparation steps are mixing, extrusion, drying/solidification and carbonization.

The composite in the desired final configuration is subjected to an activated process to develop the pore structure. Thermal activation in an oxidizing atmosphere using air, carbon dioxide, steam or a mixture of these, is generally used to carry out this step. The size of the pores depends on the type of activating agent, the temperature of activation and the burn-off degree.

4.4.3.4. Carbon films

Molecular separations based on differences in molecular size and shape are particularly important for gas separations such as the separation of N_2/O_2 from air, H_2/C_xH_y from light hydrocarbon mixtures, or CO_2/CH_4 from biogas. To make a useful membrane the separation layer must be thin ($< 50 \cdot 10^{-6}$ m) and yet have good mechanical properties to facilitate handling and fixing into separation modules. So far two types of carbon membranes have been prepared: unsupported and supported. The unsupported materials provide high selectivities but suffer from extreme fragility. This drawback can be avoided by forming carbon layers on support media such as porous graphite, sintered stainless steel and ceramic supports. Continuous carbon membranes can be prepared by the deposition and pyrolysis of a polymer on the substrate. However, the mismatch of materials, in particular the mismatched CTE's, may lead to stress cracking of the membrane, rendering it useless. Precise control of the deposition and carbonization steps is required to prepare good carbon membranes by this method. Other alternatives for carbon membrane preparation include the carbonisation of hollow polymer fibres and the vapour deposition of carbon on a porous substrate. However, these technologies also present certain problems. In the case of hollow fibres the final products are fragile and limited in form. Carbon vapour deposition is very expensive, slow and limited to line of sight coating. However, the rapid development of these technologies and further investigation will surely lead to the large scale production of carbon membranes.

4.4.3.5. Template derived carbons

Porous carbons with controlled porosity in the mesopore range have recently attracted great attention because of their potential use as advanced adsorbents in adsorption and separation systems, as catalytic supports in fuel cell electrodes and as double-layer supercapacitors for energy storage. However, the traditional methods via activation are unable to produce this type of carbons. Although different techniques for preparing mesoporous carbons can be found in the literature [59], only a few of these permit an accurate control of

mesoporosity. The most common method of preparing mesoporous carbons uses mesostructured silica materials as templates. The preparation of these materials consists of the following steps: (a) the infiltration of the porous structure of an inorganic material (template) by the carbon precursor (generally a polymer or prepolymer), (b) the polymerisation of the infiltrated substance, (c) the carbonisation of the nanocomposites formed and (d) the elimination of the template. The porous structure of the carbon materials obtained by this method are a replica of the silica skeleton. Thus, depending on the type of mesostructured silica that is used as template, carbons with different structures and pore sizes are obtained. These carbons possess a relatively high porosity ($< 1 \text{ cm}^3 \cdot \text{g}^{-1}$) formed essentially by mesopores of about $3\text{-}5 \cdot 10^{-9} \text{ m}$, with a high degree of homogeneity in their distribution and an elevated surface area.

5. REGENERATION OF EXHAUSTED ACTIVATED CARBONS

Most of the industrial processes of adsorption with activated carbon operate in a continuous way where the stream of liquid or gas that contains the adsorbate to be removed is passed through a column filled with activated carbon. As the adsorption process proceeds, the activated carbon becomes saturated with the adsorbate, which occupies the sites available for the adsorption. Eventually, the adsorption capacity of the activated carbon decreases to a level that makes it unacceptable for further utilization and so it has to be replaced by fresh activated carbon. Once the carbon is exhausted there are, at least, two options. It can be disposed of by incineration or land filling, or it can be regenerated for further reutilization. In principle, and depending on the characteristics of the process, the second option offers clear advantages such as a lower consumption of activated carbon and the possibility of recovering adsorbed products of potential economic value. However, the regeneration of exhausted carbons also implies costs that on some occasions are not much lower than the cost of the production of new activated carbon. What is worse, most of the regeneration processes give rise to a carbon with a smaller adsorption capacity than the original activated carbon. After a certain number of regeneration cycles this adsorption capacity decreases to a level where the carbon cannot be regenerated anymore. Moreover, powder activated carbon is difficult to regenerate, since most of the commercially available processes may lead to heavy losses of carbon. Regeneration is, therefore, almost exclusively carried out with granular activated carbon, which, although in greater demand costs more to produce than the powdered forms. At an industrial level, users may regenerate the spent carbon in house, or may contract an outside company, which is usually the manufacturer of the activated carbon.

Taking into account the above considerations different regeneration strategies have been developed or are under investigation. Here is a brief description of the most commonly used.

5.1. Thermal regeneration

This is one of the most frequent methods used in the regeneration of exhausted activated carbons. It consists in heating the carbon at temperatures between 873 – 1273 K in different types of furnace such as a rotary kiln, a multiple hearth, a fluidized bed, etc. so that the adsorbate is desorbed from the carbon. More recently microwave furnaces have also been used as they offer economical and environmental advantages over the classical methods of heating [60]. The thermal regeneration method is very versatile and it may be accompanied by a pressure reduction. This method permits the recovery of the adsorbed product and it is the basis of the solvent recovery process. The process is not, however, exempt from drawbacks. Thus, thermal regeneration requires relatively high energy consumption and the handling of the carbon results in a loss of material by attrition of about 5%. In some cases regeneration has to be carried out under activated conditions using steam, air, CO₂, etc. in order to decompose and desorb the adsorbed compounds and it is more properly called reactivation. Reactivation may also oxidize or burn the adsorbate to the point where it cannot be recovered.

5.2. Steam regeneration

This method is the most commonly used for adsorbates of a low boiling point and it is usually performed on-site. The main difference from thermal reactivation is that it operates at lower temperatures. Once the carbon is saturated, a steam flow is passed through the carbon bed, usually in a counter current fashion to that of the stream that previously saturated the carbon. The steam, due to its high heat content desorbs the adsorbate from the carbon and carries it out of the adsorber vessel to a heat exchanger where the mixture is condensed. This method usually permits the recovery of the adsorbate. However, for compounds soluble in water, additional processes such as steam stripping or distillation need to be used in order to separate the solvent and water and to dry the recovered solvent. A variation of this method using hot nitrogen or air instead of steam can also be employed in these cases.

5.3. Regeneration with solvents

Extraction with appropriate solvents can also be used to remove the solute from the porous structure of the activated carbons. The regeneration is carried out by passing a stream of the solvent through a bed that contains the carbon. Usually these solvents are relatively expensive, so they need to be recovered by distillation or precipitation. This also permits the recovery of the compounds previously adsorbed into the activated carbon.

5.4. Supercritical fluid regeneration

The properties of fluids under supercritical conditions are considered ideal for extracting substances from exhausted activated carbons. Two supercritical fluids are of particular interest, carbon dioxide and water. Carbon dioxide has a low critical temperature of 304 K and a moderate critical pressure of 73 bar, while water has a critical temperature of 647 K and a critical pressure of 220 bar. The character of water at supercritical conditions changes from one that supports only ionic species at ambient conditions to one that dissolves paraffins,

aromatics, gases and salts [61]. These supercritical fluids exhibit densities similar to those of liquids (high solvent strengths) and diffusion coefficients similar to those of gases (excellent transport characteristics), enabling them to effectively dissolve and/or desorb contaminants from the carbon surface and to easily enter/exit even the smallest pores and carry away any released material. On the restoration of ambient conditions, the supercritical fluid is reconverted into a gas or liquid and all formerly dissolved/desorbed substances allowing both the solvent and the solute to be recovered. One problem with this method of regeneration is that it requires equipment that is highly resistant to corrosion and able to operate under extreme conditions.

5.5. Chemical regeneration

This method implies a reaction of the adsorbate with a regeneration agent, which eliminates it from the carbon. For example, sodium hydroxide or sodium bicarbonate reacts with phenol to form sodium phenolate which is soluble in water. Acids can also be used at elevated temperatures to remove heavy metals from exhausted carbons. Treatment with these chemicals may also affect the structure of the carbon, causing changes to the porosity and in most cases impairing its adsorption capacity after a few regeneration cycles.

5.6. Biological regeneration

This method uses aerobic or anaerobic micro-organisms to remove biodegradable adsorbates. The carbon is placed in contact with a solvent, which also contains micro-organisms. The compounds are desorbed by diffusion from the pores to the solution where the micro-organisms digest the compounds, transforming them into non-toxic substances. Consequently, a low concentration of solute is maintained, which facilitates the desorption of the adsorbate. Compared with thermal regeneration, this method consumes much less energy since it operates at low temperatures. However, the main problem is that the temperature, pH and concentration of the solution need to be kept under strict control in order to keep the colony of micro-organisms at an adequate level.

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