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Nanoporous Carbon Synthesis: An Old Story with Exciting New Chapters

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Abstract

Activated carbons are key materials in technological applications of multidisciplinary fields (e.g. adsorption, separation, and catalytic processes). The extensive use of these materials results from the combination of a well-developed pore network (micropores or micro + mesopores) along with the presence of heteroatoms (e.g. oxygen, nitrogen, and sulfur). The large scale production of nanoporous carbons is a well-established process since the first patents date from the beginning of the twentieth century. Conventional activation methodologies are divided between physical, using steam or CO_2, and chemical, being KOH, $ZnCl_2$, and H_3PO_4 the most commonly reported oxidizing agents. Due to the panoply of operational parameters that can be changed or added in the production of activated carbons, there is still room for R&D. In this chapter, both conventional and innovative synthetic processes are reviewed to offer an up-to-date picture regarding raw materials, carbonization step, activation process, and other approaches. Conventional activation of gels and chars obtained by novel approaches (i.e. sol-gel method, hydrothermal carbonization (HTC), and acid-mediated carbonization) and more innovative strategies (i.e. variations of HTC process, carbonization of organic salts and ionothermal approaches) are addressed. Textural, surface chemistry and morphological properties of the derived porous carbons were reviewed and critically rationalized.

Keywords: nanoporous carbon materials, carbon precursors, conventional synthesis, innovative synthesis, pore size distribution, heteroatom doping, morphology

1. Historic perspective

Carbon is the main element of the entire world's flora, and its atomic structure allows unique bonding possibilities leading to various structures with distinct properties. As consequence, carbon materials are used for so long that it is hard to determine the very first moment.

At the beginning, carbon was used in the form of charcoal that consists of carbonized wood, coal or partially devolatilized coals, and also carbon black obtained by incomplete burning of vegetable oil. After centuries of use of these man-made forms of carbon, the discovery of the processes to perform the activation of charcoal allowed to greatly improve the properties and performances of carbon materials. These new materials where pores (voids) are enclosed by carbon atoms are known as activated carbons or active carbons and, more recently, also named as nanoporous carbons.

The oldest known man-made carbon forms—charcoal and carbon black—were used in the Stone Age as a black color pigment for cave painting [1]. For example, charcoal was used as color pigment to draw the black lines of the illustrations in the Cave of Altamira (Spain) that represents the apogee of Paleolithic cave painting art developed across Europe, from 35,000 to 11,000 BC. At about 8,000 BC, charcoal was used in metal production [1]. In 3,750 BC, the Egyptians and Sumerians used it in the reduction of copper, tin, and zinc minerals in the bronze manufacturing process and also as smokeless fuel [2–4]. The first proof of the medicinal use of carbons was found in an Egyptian papyrus, dated of 1,550 BC, where it is reported the use of charcoal for the adsorption of odors from putrefying wounds and also to treat problems of the intestinal tract [5, 6]. The therapeutic value of carbon was later explored by the Greeks (Hippocrates, ca. 460–370 BC) and Romans (Pliny the Elder, AD 23–79) in the treatment of various diseases, including food poisoning, epilepsy, chlorosis, and anthrax [1, 7]. Hippocrates also recommended that the water should be filtered with carbonized wood before its consumption, so as to eliminate bad flavor and odor [8]. Also, Hindu documents from 450 BC mention the use of sand and charcoal filters for drinking water purification [5, 6]. Recent studies also concluded that in Phoenicians ships (460 BC) drinking water was stored in carbonized wood barrels to keep it fresh, a practice that was continued until the eighteenth century. In 157 AD, a medical treatise from Claudius Galvanometer indicated the use of carbons of both vegetable and animal origin for the treatment of various diseases [9]. A Sanskrit document (AD 200) recommended that after being stored in copper vessels and exposed to sunlight, water should be filtrated with coal [6]. This is most probably one of the earliest manuscripts describing the degradation of contaminants from water to assure its disinfection.

It was only during the eighteenth century that the mechanisms underlying the properties of charcoals started to be recognized. In 1773, Scheele measured the adsorptive properties of charcoals from distinct sources using various gases; a decade later, Lowitz studied the abilities of charcoals to adsorb odors from wounds [7, 9]. This author published results regarding the adsorption of a range of organic vapors and also studied systematically the adsorption in various aqueous solutions, namely in the decolorization of contaminated tartaric acid solutions. The discussion of the contribution of charcoals to control odors from gangrenous ulcers was made by Kehl, in 1793, who also discovered that charcoal from animal origin (animal tissues) could be used to remove color from solution, including from sugar solutions [7, 9]. The introduction of carbon materials in industrial processes took place in England, in 1794, when wood charcoals were applied as bleaching agents in the processing of sugar. By that time, the method for preparing the wood charcoals was kept a secret [9]. In 1805, the first large-scale sugar refining facility was introduced in France by Gruillon, working with ground and washed wood char [9]. Between 1805 and 1808, Delessert demonstrated the effectiveness

of charcoal for decolorizing sugar-beet liquor contributing for the growth of this industry in France [9]. In 1808, all European sugar refineries were using charcoal as a decolorizer [9]. The discovery of bone-derived char as a more efficient raw sugar syrups decolorizing agent was made by Figuier in 1811, and quickly the sugar industry replaced wood charcoal by this improved material [5, 9]. The regeneration of bone-derived char by heating was discovered in 1811, and sometime later granular bone-derived char started to be produced, thus enabling an easier regeneration [9]. In 1815, the majority of sugar refining facilities were using granular bone-derived char [9]. The dependence of the decolorizing properties on the char's source, the thermal processing and particle size was demonstrated by Bussy in 1822 [9]. He also produced a carbon material with higher decolorizing ability than bone-derived char by heating blood with potash, being this the first recorded example of an "activated carbon" material obtained by thermal and chemical processes [5, 9].

The first large-scale application in gas phase took place in 1854 [8], with the installation of carbon filters in London sewage ventilation systems. In 1872, carbon filters were also used in the masks of the chemical industry workers for preventing the inhalation of mercury vapors.

Besides thousands of years of history, and the already large range of applications for charcoals, it was only in the beginning of the twentieth century that one of the most outstanding abilities of carbon materials was explored: the possibility of enclosing a huge porosity into the carbon material structure. This "revolution" was due to the discoveries of Raphael von Ostrejko that, between 1900 and 1903, patented two different methods for the industrial activation of charcoal and the production of activated carbon materials [10]. This set of patents mentions the bases of the chemical activation process (carbonization of lignocellulosic materials with metallic chlorides) and of the thermal or physical activation (slight gasification of chars with water vapor or carbon dioxide at elevated temperatures) and also the specific equipment for thereof. The factory for full-scale activated carbon production was built by that time in Ratibor, now named Raciborz (Poland), and still operates, being so the world's oldest industrial activated carbon manufacturing plant [10, 11].

Although sugar industry was the first to apply activated carbons, in this case for whitening purposes, the starting point for the great development in the production and application of activated carbons was undoubtedly World War I, when these materials were used in gas masks [7, 8]. The production and search for new activated carbons has been boosted decade after decade due to their fundamental role in various technological applications which are related to, namely, restricted environmental regulations, recovery of valuable chemical compounds, and catalysts support [8, 12–14].

Nowadays, the driving forces for the research in nanoporous carbons are related with the properties of the most recent carbon materials: fullerenes [15], carbon nanotubes [16] and graphene [17]. However, the excellent properties of these novel carbon forms also fostered the interest in the traditional porous carbons and, in the recent years, a considerable number of studies searching for new synthetic approaches have been published. The main objective is the preparation of highly porous materials with controlled porosity, and often also with tuned surface chemistry, to present enhanced behavior as, for example, electrode materials for supercapacitors.

2. Properties of nanoporous carbons

Describing nanoporous carbon materials as carbon structures with enclosed porosity is correct but it is somewhat incomplete since properties, as for example, surface chemistry, chemical composition, morphology or electrical conductivity are also essential to understand their potential and performance in a given application.

Regarding the physical properties of nanoporous carbon materials, porosity is undoubtedly the most important one. IUPAC defines *nanopores* as pores with apertures up to around 100 nm and, according to their size, *nanopores* are classified as follows [18]:

- *Micropores*—pores with width less than 2 nm

- *Mesopores*—pores with width between 2 and 50 nm

- *Macropores*—pores with width greater than 50 nm

Due to their relevance for the adsorption process, micropores can be further distinguished between *narrow micropores* (i.e. *ultramicropores*) with width <0.7 nm and *wide micropores* (i.e. *supermicropores*) with width between 0.7 and 2 nm [18].

The limits for this pore classification were suggested by nitrogen adsorption-desorption data at −196°C [18] and rely on the fact that each pore size range corresponds to different pore filling mechanisms disclosed by the isotherm profile [19]. Micropore filling is regarded as a primary physisorption process and occurs at low relative pressures. Firstly, at very low relative pressure, adsorption occurs in the ultramicropores where due to the close vicinity of pore walls there is an overlapping of the adsorption forces favoring the enhancement of the adsorbent-adsorbate interaction, this process is termed "primary micropore filling." After this initial filling in the most energetic sites, the cooperative adsorbate-adsorbate interactions inside the supermicropores become more relevant (secondary process) occurring up to relative pressures ≈ 0.15 [18]. In mesopores, the physisorption comprises three stages: monolayer adsorption (i.e. all adsorbate molecules are in contact with the surface of the adsorbent) followed by consecutive adsorbate layers (multilayer adsorption) and finishing with capillary condensation [18]. The adsorption onto mesopores commonly presents a hysteresis loop [19]. The macropores are so wide that do not allow capillary condensation since behave as an open space (cannot be characterized by nitrogen adsorption whose maximum relative pressure occurs near the unity) [19].

In nanoporous carbons, the porosity results from the voids between the randomly cross-linked graphite-like crystallites that constitute the structure of the carbon skeleton, from the consumption of less organized carbonaceous matter and also from the removal of reactive carbon atoms in the crystallite during activation process (**Figure 1**). Surface area and pore size distribution (PSD) are the physical properties that will greatly influence the performance of nanoporous carbons in a given process. These parameters are commonly obtained from the analysis of nitrogen adsorption isotherm at −196°C. The surface area (apparent surface area for microporous materials) is commonly obtained applying the Brunauer-Emmett-Teller (BET) equation. Regarding
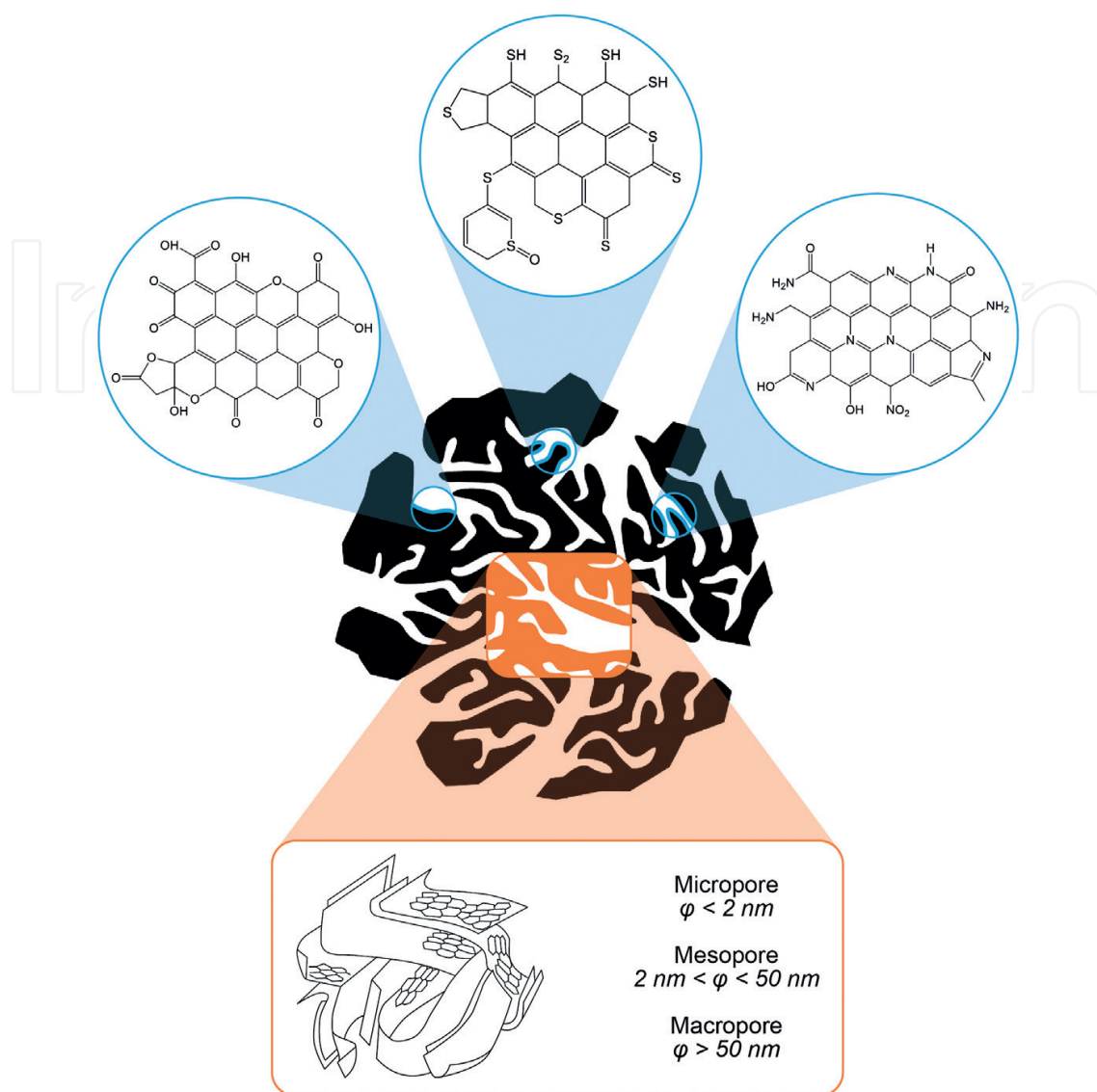
Figure 1. Schematic representation of pore structure (bottom rectangle) and surface chemistry—oxygen, nitrogen, and sulfur groups (top circles)—in nanoporous carbons.

the PSD, there are various mathematic models available, being those using the Non-Local Density Functional Theory (NLDFT) the most advanced ones. The use of nitrogen as adsorptive at −196°C has however diffusional limitations in ultamicroporous carbon materials; thus, for an accurate characterization of the micropore network, carbon dioxide adsorption at 0°C has been repeatedly proposed as a better alternative to nitrogen [20–22]. Besides the limitation of nitrogen for the characterization of ultramicropores, it is known that, due to its quadrupole moment, nitrogen molecule orientation during adsorption will be dependent on the surface chemistry of the adsorbent [18, 22]. To overcome this issue, other adsorptive gases like argon or krypton can be used.

Carbon atoms are the major element of nanoporous carbon skeleton but the elemental composition of these materials also includes hydrogen and oxygen and, depending on the precursor, preparation route and post-synthesis functionalization may also have nitrogen,

sulfur or phosphorus containing groups. These heteroatoms are mainly located at the edges of the basal planes due to the presence of unsaturated carbon atoms that are highly reactive. **Figure 1** summarizes the most relevant oxygen, nitrogen, and sulfur-containing surface groups that may be present in the surface of nanoporous carbon materials, being important to mention that oxygen surface groups are, by far, the most common ones. These materials may also contain inorganic matter, sometimes attaining 20% (wt.), being this ash content mainly inherited from the carbon precursor [12].

The elemental composition and type of surface groups of a nanoporous carbon influence its performance in both gaseous and liquid phase processes, due to specific interactions with the adsorptive and also the solvent in the case of adsorption from solution. Properties like hydrophobicity/hydrophilicity or acid/base behavior are highly dependent on the surface chemistry of these materials. Carbons are in general hydrophobic, but the presence of increasing amounts of oxygen surface functionalities favors the adsorption of water molecules due to the formation of hydrogen bonds and, consequently, its wettability. This ability of porous carbon materials may be advantageous, or not, depending on the desired application. For example, in the impregnation of carbon supports with catalysts in aqueous phase, a high wettability will increase the impregnation degree; but in the adsorption of organic compounds from diluted aqueous solutions, higher wettability may led to the formation of water molecule clusters that hinder the diffusion of the target compounds towards the adsorption active sites (the same being valid for gas steams purification).

Regarding acid/base character, nanoporous carbons are considered amphoteric materials due to the presence of both acid and basic sites in their surface. Thus, depending on the amount and strength of all the surface groups, the materials may present net acid, basic or neutral surfaces. The surface chemistry of nanoporous carbons can be assessed through numerous techniques, and the best way to get a good characterization is to employ complementary techniques and combine the analysis of the results. For example, Boehm and potentiometric titrations provide qualitative and quantitative information on the surface of the nanoporous carbons, while temperature programmed desorption (TPD) detects more oxygen groups than Boehm titration, although with less quantitative information. On the other hand, X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared spectroscopy (DRIFT) provide qualitative information about the surface of the nanoporous carbons [23].

Other properties of nanoporous carbon materials that may play important roles in specific applications are the morphology (powdered (PAC) and granular (GAC) forms are the most common ones), electrical conductivity, hardness and density.

For more specific information regarding properties of nanoporous carbon materials and characterization methods, several reference texts are available [8, 21, 23–27].

3. Nanoporous carbon synthesis

There are a large range of carbon-rich precursors namely from vegetable (e.g. wood, fruit shells, stones or peels) or petrochemical origin that can be successfully transformed into activated carbons. However, the economically viable large-scale production of activated carbons

requests the use of raw materials that gather high availability and constancy with high density and hardness, low inorganic content and, last but not the least, low cost. Thus, commercially available activated carbons are mainly produced from coal (i.e. lignite, sub-bituminous, bituminous and anthracite), coconut shell charcoal and wood charcoal. The raw material is a key issue for activated carbon producers since the development of the porous network occurs by consumption of the (char)coal precursor and the preparation yields can reach values as low as 10% (wt.). Consequently, assuring the supply of high quality precursors at a cost-effective price is of paramount importance to control the quality of the final material and the production cost. In 2015, the global activated carbon market was valued by Markets and Markets at USD 4.74 billion corresponding to 2743.7 kton being expected to continue to growth, mainly driven by more stringent government regulations to assure human and environmental protection. As already mentioned, (char)coal is the most important raw material for activated carbon producers but they are not the major (char)coal consumer. In fact, activated carbons are only a "by-product" of (char)coal production, which have the energy sector as major market (mainly for metallurgical, industrial and cooking fuel) that actually controls demand and prices. This reality, allied to the fact that most of raw materials came from the Asian continent, and that external factors (e.g. natural disasters) may compromise the quality, availability and cost of (char)coal, continues to drive the research for finding new, and more sustainable, raw materials and preparation routes for activated carbon production.

Conventional methods for activated carbon production request the use of high temperature kilns where, under a controlled atmosphere, the carbon-rich raw materials are transformed into nanoporous carbons. There are numerous procedures for the production of activated carbons, although the great majority of synthetic routes published and patents registered worldwide, including those allowing nowadays industrial production, fall in two major categories: the selective gasification of raw materials' carbon atoms (physical or thermal activation), and the co-carbonization of the precursor with oxidizing and/or dehydrating agents (chemical activation). The number of steps requested for the production of activated carbons depends on the characteristics of the raw material, morphological specifications of the final product, and on the type of activation. A general process flowsheet is presented in **Figure 2**.

The most commonly used **pre-treatments** are those aiming to obtain a given particle size or shape, washing steps for dirt removal and/or for the reduction of the inorganic content (i.e. acid washing) and pre-oxidation to prevent fluidization of coking coal during carbonization [8, 12]. The raw material can be crushed and sieved to obtain powdered or granular particles with specific dimensions. Milling, binder addition and briquetting are other common options when working with precursors presenting low volatile content (e.g. medium-high rank coals,
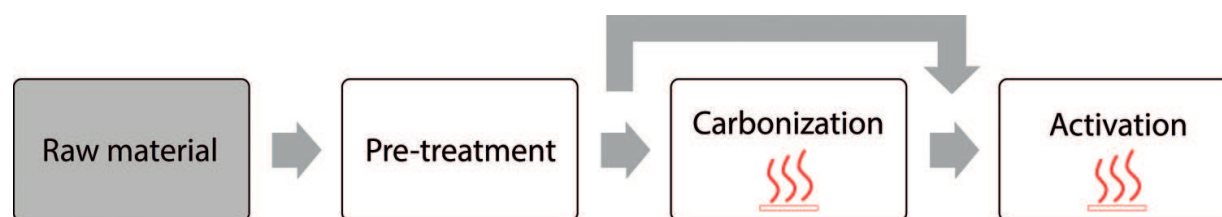
Figure 2. General flowsheet for conventional physical (thermal) and chemical activation processes.

volatiles <20–30% (wt.)). To assure an efficient diffusion of the activating agent to all the individual coal particles of the briquette, it is common to mill and subsequently briquette the particles to obtain granular materials with a well-developed network of transport pores (i.e. meso and macropores) [8]. Direct activation of granular coal with low volatile content will not allow an uniform activation of the granules due to the incipient network of transport pores.

Physical or thermal activation is generally made in two consecutive heating steps: carbonization under inert atmosphere (usually nitrogen) to devolatilize the raw material, followed by activation that consists in the partial gasification of the obtained char with oxidizing agents (i.e. steam, carbon dioxide or a mixture of both) leading to the formation of the porous network. While the carbonization usually occurs at temperatures between 400 and 600°C, the gasification requests temperatures ranging from 800 to 1000°C. Depending on the raw material, it is also possible to avoid the carbonization step and proceed directly to the thermal activation. Activation with CO_2 must occur in conditions that assure chemical control (slow activation rate—days) instead of diffusional control which is faster but leads to external particle burning and, consequently, to poor porosity development [8]. The reactions of steam and carbon dioxide with carbon are endothermic, thus thermal activation needs external energy supply to maintain the requested high temperature. Oxygen (or air) is not commonly used as oxidizing agent since its reaction with carbon is highly exothermic and fast, being difficult to control and assure porosity development instead of particle consumption [8, 12, 24]. Due to this and to the safety issues related to the temperature control, oxygen activation is scarcely used. However, low amounts of oxygen (or air) can be added during thermal activation with steam or carbon dioxide to help maintaining the high temperatures by reacting with the gases produced during activation (i.e. CO and H_2) [24]. This approach has the advantage of lowering the pressure of CO and H_2, both inhibiting gases for the activation, and increasing the partial pressure of the activating agent [24].

Chemical activation usually requests only one heating step: the raw material is mixed with an activating agent (e.g. $ZnCl_2$, H_3PO_4, KOH) and is further treated under controlled atmosphere at temperatures from 400 to 900°C, depending on the selected activating agent. The solid product obtained need to be exhaustively washed with water to remove the chemicals and dried before storage. In this process, the mechanism of pore formation is dependent on the chemical agent: zinc chloride promotes the removal of water molecules from the lignocellulosic structures of the raw material while phosphoric acid combines chemically with them [24]. In none of these processes, the selective removal of carbon atoms occurs. With potassium hydroxide, the process is more complex since there is the disintegration of the structure followed by intercalation of the metallic potassium [24, 28, 29] into the "graphitic" laminar structure, breaking down particles and limiting granular activated carbons synthesis. Simultaneously, there is also some gasification of carbon atoms due to reaction with CO_2 and H_2O, resulting from the redox reaction of carbon with potassium compounds [30]. During carbonization (i.e. heat treatment under inert atmosphere), the lignocellulosic precursor losses volume by contraction, but when chemical activation is applied there is incorporation of the activating reagent inside the particles inhibiting the expected contraction, that is, the activating agent may behave as a template for the formation of the microporosity [24]. In fact, in 2004, Molina-Sabio and Rodríguez-Reinoso [30] published an enlightening research that allowed to conclude that the dehydration of the carbon precursor (i.e. peach stones) by $ZnCl_2$

occurs along with templating by the activating agent, thus justifying the porosity evolution with the amount of $ZnCl_2$ impregnated.

Chemical activation has advantages over physical process related with the use of a single heating step and lower temperatures, usually higher yields, shorter activation time (hours) and higher surface area and pore volumes. All these add-ons came with a price since this activation process is more corrosive (e.g. $ZnCl_2$ or KOH) than the physical one, and activating agents can be hazardous for the environment (i.e. $ZnCl_2$ and H_3PO_4). Also, regardless the activating agent, a time-consuming washing step is needed to remove chemicals from the newly formed pore network and, if possible, to recover the activating agent. Actually, $ZnCl_2$ use is declining due to the environmental issues associated with zinc residues [12], low recovery efficiencies, corrosion problems and presence of residual zinc in final carbon [8].

Zinc chlorine and phosphoric acid lead to higher activation yields ($\approx$40%) compared to physical activation since the use of these compounds inhibit the formation of tar and other by-products formed in physical activation [12]. In the case of potassium hydroxide, the more complex activation mechanism gathering K intercalation in carbon lattice and gasification allows to prepare activated carbon with a large range of yields depending on the precursor: from 80 and 70% [31–33] to values, as low as, 20–10% [34–36]. KOH allows obtaining superactivated carbons (over 3000 m^2 g^{-1}) when high KOH/precursor weight ratios (i.e. between 2 and 4) are used.

Table 1 gathers information regarding the most suitable precursors for the commonly used activating agents, as well as, the type of porosity obtained, and the effect of experimental conditions on the pore size distribution. It is important to emphasize that the effect of experimental conditions on pore size distribution presented in **Table 1** is a general trend; thus, for an in-depth knowledge of the effect of activating agent and experimental conditions on the porous characteristics of a given raw material, a comprehensive study is always needed.

The above-mentioned precursors and activating agents are those more representative for industrial scale production of activated carbons. However, regarding the production of specialty carbons (low volume processes) and for research works, the number of options increases exponentially. Regarding raw materials, hard biomass residues like shells and stones allow to obtain high quality PACs or GACs; phenol formaldehyde polymers yield high surface area porous carbons, while polyacrylonitrile (PAN), acrylonitrile textile or rayon are adequate to synthetize activated carbon fibers or cloths [24]. When aiming nitrogen doped materials, for example for the adsorption of sulfur species, the use of polymers containing nitrogen (e.g. PAN) is a common synthetic route. In what concerns activating agents, besides $ZnCl_2$, H_3PO_4 and KOH, alkali hydroxides and salts (e.g. NaOH, K_2CO_3, Na_2CO_3) and metal chlorides (e.g. $AlCl_3$, $FeCl_3$, NH_4Cl, $CuCl_2$) can also be used [24].

At industrial scale, steam activation continues to be the most widely used method to produce activated carbons. The advantages of steam activation are related with the fact that does not request post-activation work-up, namely a final washing step, is less expensive and has less environmental constrains than the chemical activation. Besides, for precursors with less than 10% of ash, carbon materials with surface areas of 1000 m^2 g^{-1} can be easily obtained with activation yields of 50% [8], thus allowing a good compromise between production cost and porosity development.

Type of activation	Activating agent	Appropriate precursors	Porosity	General trend of experimental conditions on pore size distribution (PSD)
Physical	CO_2	Coals and, in less extend, hard lignocellulosic materials	Micro	- High activation degree leads to high volume of micropores with similar pore size distribution (PSD)
	Steam	Coals and, in less extend, hard lignocellulosic materials	Micro (+ meso)	- Widening of PSD with increase in activation degree - Micro + mesopore networks are obtained at high activation degree (yield 20%) and/or high activation temperatures
Chemical	$ZnCl_2$	Lignocellulosic materials (high volatile and oxygen content)	Micro + meso	- Uniform microPSD that widens to the border of micro/mesopore with the increase of Zn/precursor ratio
	H_3PO_4	Lignocellulosic materials (high volatile and oxygen content)	Micro + meso	- PSD mainly in the border of micro/mesopore and dependent on heat treatment temperature (<450°C)
	KOH	High rank coals (low volatile and high carbon content)	Micro	- KOH/precursor ratio has more influence on adsorption capacity and PSD than activation temperature - Increase of KOH/precursor ratio widens pores from narrow to large micropores and, in less extend, to small mesopores; also hinders the granular morphology (particle disintegration leads to powders)

Table 1. Appropriate precursors, kinetic of activation, and type of porosity usually obtained for the most common activating agents (information gathered from reference literature [8, 12, 24, 29]).

In general, the above-described activating methodologies produce activated carbons with wide pore size distributions, so the need for carbon materials with more regular porosity prompted the research on the synthesis of ordered mesoporous carbons (OMCs) by applying hard or soft templating approaches. The advantages of OMCs over conventional activated carbons are related with the ordered and hierarchical pore network, but their multi-step preparation procedures are time consuming, use hazardous chemicals to remove the inorganic templates and, consequently, have very low atomic economy and high production costs. This class of nanostructured materials is out of the scope of the present chapter since the first works were published in the late 1990s, and comprehensive reviews are available in the literature, providing a broad overview and up-to-date information on synthesis and properties of this class of porous carbon materials [37–39]. In the following, the recent developments regarding new synthesis approaches—i.e. precursors, activating agent and routes—for preparing nanoporous carbon materials are presented.

3.1. Conventional activation of gels and chars obtained by novel approaches

As already mentioned, classical preparation of activated carbons usually requests an initial thermochemical process (carbonization) to remove other elements than carbon and transform

the raw material (i.e. coal or biomass) in a carbon-rich material (charcoal) that will be subsequently activated to improve the pore network. This thermochemical conversion is particularly important when using biomass whose carbon content usually is between 30 and 50% (wt.) [25]. However, the need for more specialized porous carbon materials, as well as the growing interest in developing more sustainable and greener processes, has prompted the research community to explore alternatives to the conventional carbonization step which, in some cases, also allow to make feasible the use of novel precursors.

In the category of alternative methods to obtain carbon-rich materials for further activation *via* conventional methodologies, processes as distinct as sol-gel polymerization reaction, hydrothermal carbonization (HTC) and acid-mediated carbonization (AMC) can be grouped. While sol-gel process involves the use of synthetic compounds—resorcinol and formaldehyde—as reagents for the polycondensation reaction in the presence of a catalyst, both HTC and AMC are mainly applied to transform biomass into a coal-like material.

The first resorcinol-formaldehyde organic gel was synthetized by Pekala in 1989 being the aqueous polycondensation performed under alkaline conditions [40]. One of the major advantages of this process is its flexibility since the main properties of the gel can be tuned during the synthesis and drying process. The synthesis starts with the formation of the wet gel and, during this step, the most important parameters controlling the properties of the final gel are the precursors' concentration, the catalyst type and concentration and the time and temperature of curing [41]. After drying, aerogels (supercritical drying), xerogels (subcritical drying), and cryogels (freeze drying) can be obtained. The drying procedure is one of the most important steps regarding the porous properties of the organic gel and is also crucial when the preparation of a thermally stable carbon gel is foreseen. The organic gels are mainly mesoporous materials thus if the preparation of a micro + mesoporous material is envisage a thermochemical step involving carbonization and/or activation must be considered. The first works focused on the carbonization and activation of organic gels were published during the 1990s, and nowadays, these methodologies continue to be studied to better tune the pore network of these materials and explore novel applications.

A great advantage of conventional activation of organic gels over the previously mentioned carbon precursors is the possibility of coupling the mesopore network of the organic gels with micropores created during carbonization or activation step. Tamon et al. studied the effect of carbonization on the porous properties of aerogels and cryogels proving that both precursors preserved the mesoporous structure after the thermal treatment and that cryogels are more prone to develop micropores [42]. Regarding activation, literature data reveal that the gasification of aerogels with CO_2 allows retaining the mesopore network of the organic gels and increasing the volume of micropores [43, 44]. Moreno-Castilla and co-workers reported the activation of a mesoporous aerogel with CO_2 showing that for a 22% burn-off the increase and widening of the precursor micropore network practically did not change the mesopore structure [44]. In a recent work, Ania and co-workers [45] evaluated the effect of carbonization and activation (physical and chemical) of xerogels which, due to their drying in subcritical conditions, may suffer stronger changes upon thermal treatment. In fact, both carbonization and CO_2 activation lead to the increase of the micropore volume at the expense of a severe

decrease in the mesopore volume and shrinkage of the average pore size. However, under controlled experimental conditions (i.e. impregnation methodology and temperature), the chemical activation of the xerogel with KOH or K_2CO_3 allowed to suppress the shrinkage and structural collapse, forming a micropore structure associated with the enlargement and/or preservation of the mesopore network of the pristine xerogel [45]. For further discussion and information regarding the control of the properties of resorcinol-formaldehyde organic and carbon gels, the reader can refer to the reviews by Al-Muhtaseb and co-workers [41, 46].

Hydrothermal carbonization (HTC) is probably one of the most promising alternatives to conventional carbonization of biomass, as it is clearly shown by the ever-increasing number of publications focused in this process since the beginning of the twentieth century. HTC is inspired in the natural processes of coal formation that take millions years and request temperature and pressure in a nonoxidizing atmosphere to transform biomass into a carbon-rich material. Interestingly, the first research work on HTC was published in 1913 by Friedrich Bergius, a Nobel Laureate in recognition of his studies regarding carbon-water reactions at high pressure and mild temperature to successfully produce H_2 by avoiding CO generation [47]. When performing the experiments, Bergius noticed that when peat was used as carbon source the solid residue obtained had an elemental composition similar to that of coal, leading him to investigate the HTC decomposition of plant-based compounds into coal-like materials [48]. As reported in [49], with the exception of the works by Berl and Schmidt (1932) and van Krevelen et al. (1960), the interest in the solid carbon materials obtained from HTC process was forgotten until the work published by Wang et al. [50] in 2001. These authors reported the synthesis of carbon spheres from sugar under hydrothermal conditions (190°C and self-generated pressure in a high-pressure vessel). HTC is a cost effective and eco-friendly process; since to convert biomass into carbon-rich materials, it uses water as solvent, mild temperatures, self-generated pressure and occurs in few hours with no CO_2 emission. Since 2001, the interest in this carbonization process has been exponentially increasing, and in 2016, around 400 papers mentioning hydrothermal carbonization were published, and the works focusing in this process received more than 11,000 citations (source Web of Science, Sept 2017). Some advantages of HTC-derived materials, commonly known as hydrochars, over charcoals obtained by conventional carbonization is their high content in oxygenated groups and the possibility of morphological control (e.g. spherical morphology).

Hydrochars have an incipient pore network; thus, conventional activation has been commonly employed to obtain specialized nanoporous carbon materials, mainly regarding surface functionalization, morphology features and ultrahigh surface areas and pore volumes. The use of hydrochars as activated carbon precursors was first reported by Zhao et al. [51] aiming to prepare a nitrogen-containing porous carbon material to be used as supercapacitor. The authors performed HTC of D-glucosamine (carbon source) and the hydrochar containing 6.7% of nitrogen was further activated with KOH allowing to obtain a nitrogen-doped porous carbon with a BET area of 600 $m^2\,g^{-1}$.

As it can be clearly seen in the overview of hydrochar-derived activated carbons presented in **Table 2**, the great majority of studies concerning hydrochar activation used KOH as activating agent, mainly because, in general, this oxidizing agent allows obtaining the most developed microporosities reaching BET surface areas higher than 3000 $m^2\,g^{-1}$. It is also interesting to notice that there are studies reporting the use of hydrochars for the synthesis of micro + mesoporous

Activating agent	Carbon precursor	BET area (m² g⁻¹)	Observations	Ref.
ZnCl₂	*Salix psammophila*	839–1308		[68]
	Coconut shell (+ H₂O₂)	1652–1744	V_{Meso}/V_{Total} = 50–60%	[52]
	Sewage sludge	417–519	V_{Meso}/V_{Total} = 53–66% and N,S-doped	[53]
	Tobacco stem	297–1347		[69]
H₃PO₄	Glucose, sucrose	1750–2120	Spherical particles	[60]
	Rattan sawdust (*Calamus gracilis*)	1151		[70]
KOH	D-Glucosamine	600	N-doped	[51]
	Glucose	1283	Spherical particles	[59]
	Starch, cellulose, sawdust	1260–2850		[71]
	Furfural, glucose, starch, cellulose, eucalyptus sawdust	1200–2370		[72]
	Potato starch, eucalyptus sawdust (+ melamine)	3280–3420	V_{Meso}/V_{Total} = 50–55% and N-doped	[56]
	Cellulose, potato starch, eucalyptus sawdust	2125–2967		[73]
	Glucose, cellulose, rye straw	891–2250	Controlled PSD	[58]
	Spruce and corncob hydrolysis products	2220–2300		[74]
	Hazelnut	1700		[75]
	Paper pulp mill sludge	1470–2980	Sponge-like particles	[76]
	Sucrose	1169–2431	Controlled PSD	[35]
	Glucose, sucrose	1312–3152		[60]
	Jujum grass, *Camellia japonica*	1050–3537		[77]
	Bagasse waste + sewage sludge	2296	Hierarchical porosity	[78]
	Sucrose	1635–3036		[79]
	Sucrose	1534		[80]
	Tobacco rods	1761–2115	V_{Meso}/V_{Total} = 79–89% and N-doped	[54]
	Eucalyptus sawdust, *Paeonia lactiflora* (flowering plant) *Sargassum fusiforme* (seaweed)	1202–2783		[81]
	Tobacco stem	217–501		[69]
	Microalgae (*Spirulina platensis*) + glucose	1260–2370	N-doped	[63]
	Algae (*Nannochloropsis salina*) + glucose	747–1538	N-doped	[62]
NaOH	Glucose, sucrose	532–2129	Spherical particles	[60]
	Palm date seed	1282		[82]
	Rattan stalks (*Lacosperma secundiflorum*)	1135	V_{Meso}/V_{Total} = 72%	[55]

Activating agent	Carbon precursor	BET area (m² g⁻¹)	Observations	Ref.
K₂CO₃	Sucrose	694–1375	Spherical particles and controlled PSD	[35]
	Salix psammophila	964–1469		[68]
	Golden shower pods	812–903		[83]
	Tobacco stem	355–553		[69]
CO₂	Pinewood sawdust and rice husk	292–569		[84]
	Sunflower stem, walnut shells, olive stones	379–438		[85]
	Glucose, sucrose	923–2555	Spherical particles	[60]
Steam	Starch (+ acrylic acid)	785–1148	Spherical particles with blackberry morphology	[61]
	Sucrose	814	Spherical particles	[35]
Air	Sunflower stem, walnut shells, olive stones	213–434		[85]
—	Bamboo shoots (+ H₂SO₄ conc.)	972	V_{Meso}/V_{Total} = 46–54% and N-doped	[57]

V_{Meso} and V_{Total}, microporous and total pore volume, respectively; PSD, pore size distribution.

Table 2. Overview of the properties of hydrochar-derived activated carbons (2010–2017).

materials *via* chemical activation with zinc chloride [52, 53] or hydroxides [54–56], with the mesopore volume corresponding to at least 50% of the total pore volume, i.e. textural characteristics that are not easy to obtain by the most conventional carbonization + activation process. A recent work reports the preparation of an N-doped nanoporous carbon with similar volumes of micro and mesopores and a BET area near 1000 m² g⁻¹ by using HTC of bamboo shoots in the presence of water and 0.5 cm³ of H₂SO₄ followed by the carbonization of the obtained hydrochar, so in the absence of any activating agent [57]. The work by Fuertes and Sevilla enables the synthesis of superactivated porous carbons with 50% of mesopores by adding melamine during the HTC process, thus the final materials also present 1.3–1.7% of nitrogen [56]. Besides opening the possibility of preparing mesoporous carbon materials, the use of hydrochars as activated carbon precursors also allows better control of the micropore size distribution [34, 35, 58].

When starting from simple carbohydrates, the use of HTC followed by activation may enable preparing carbons with spherical morphology (diameters in the micrometer range) and smooth surfaces [34, 35, 59, 60]. It is also possible to obtain a nanoporous carbon material with spherical shape, but with blackberry morphology, by adding acrylic acid to starch during the HTC step [61].

The use of water as solvent constitutes a major advantage of HTC over convention carbonization that requests dry biomass. In fact, HTC makes feasible the use of wet biomass as is the case of algae [62, 63] or sewage sludge [53] that after being carbonized can be activated to obtain a carbon material with well-developed pore structure and also heteroatom-rich surface (i.e. nitrogen and sulfur). HTC is, in fact, a valuable process when envisaging heteroatom-doped carbon materials, since if precursors with nitrogen and/or sulfur—e.g. glucosamine, algae, sewage

sludge, tobacco rods or bamboo shoots—were selected this methodology allows retaining higher percentages of heteroatoms compared to conventional carbonization, and thus assures relevant amounts of these atoms after the activation step [53, 54, 57, 62, 63].

Following a somewhat different approach, White et al. reported the preparation of nitrogen-doped carbogel materials by reacting glucose and ovalbumin (secondary biomass precursor) in HTC conditions [64]. The novelty was the saturation of the monolithic hydrochar with ethanol followed by extraction under supercritical conditions, resembling the last step of the synthesis of organic aerogels. The final material was obtained after carbonization (350–900°C). When using 550°C, a material with an interconnected 3D pore system, BET area of 476 $m^2\ g^{-1}$ and 5–7% (wt.) nitrogen content was obtained.

Very recently, Sevilla et al. proposed an alternative to KOH activation of biomass-derived hydrochars by using potassium oxalate ($K_2C_2O_4$) and melamine to obtain N-doped superactivated carbons with high yields (40–46%) [65]. The materials attained BET areas near 3000 $m^2\ g^{-1}$, presenting mainly micropores (70%) and nitrogen content between 0.5 and 0.9% irrespectively the amount of melamine used. Although the mixture of potassium oxalate/melamine is presented by the authors as an alternative to the corrosive KOH, it is important to highlight that this synthesis route is restricted for lab-scale (under restricted security conditions) since the KCN present in the solid will generate dangerous toxic vapors of HCN during the washing with HCl.

For a deeper overview regarding the HTC process and derived carbon materials, a recent book chapter by Titirici et al. [48] and a minireview [66] are recommended, and for deeper analysis on hydrochar-derived activated carbons, the following review [67] can be consulted.

Acid-mediated carbonization (AMC) is so far the less studied alternative method to obtain a carbon-rich material. However, considering that acid catalysis is a common practice to extract sugars from lignocellulosic biomass [86] and that, as just discussed, sugars can be successfully used as activated carbon precursors (i.e. *via* HTC followed by activation), this process must also be explored. This methodology allows processing largely available and hopefully low cost biomass residues. Moreover, AMC occurs at atmospheric pressure and, in some cases, at low temperature (≈ 100°C) allowing processing carbon precursors that do not gather the adequate properties to be carbonized through the conventional process or by HTC. In fact, AMC is able to maximize the availability of cellulose and hemicellulose in carbon precursors with high inorganic content (e.g. rice husk) [87, 88] and is also efficient for producing carbon-rich materials from liquid carbon precursors, as is the case of glycerol [89]. Depending on the acid catalyst used (e.g. H_2SO_4 and/or H_3PO_4), the obtained oxygen-rich chars also contain relevant amounts of sulfur or phosphorus groups, thus enhancing the reactivity for subsequent activation and allowing to join a well-developed pore network with heteroatom doping in the final activated carbon.

Wang et al. evaluated sulfuric acid hydrolysis of rice husk followed by the dehydration, polymerization and carbonization of the sugars to yield chars, which can be named as acid-chars. These materials were activated with H_3PO_4 [87, 88] and KOH [88] to produce nanoporous carbons with BET areas higher than 2400 $m^2\ g^{-1}$, and in the case of phosphoric acid activation, materials with micro + mesopore networks. In 2010, the authors reported the effect of H_2SO_4 concentration during carbonization step, as well as the reaction temperature and time onto the

yield of the obtained acidchar that attained 32% (wt.) for the reaction at 95°C during 10 h when 72% H_2SO_4 solution was used in both hydrolysis and carbonization [88]. Regarding the effect of the H_2SO_4 concentration (42–72%) during acid carbonization onto the textural properties of the activated carbon obtained by H_3PO_4 activation, the authors concluded that although acidchars prepared under distinct acid concentrations present similar elemental analysis, the BET area and pore volumes increase as the concentration of the H_2SO_4 decreases [87]. These findings were rationalized by the authors considering that high H_2SO_4 concentrations promote the aggregation of carbon nanoparticles during carbonization, limiting the uniform H_3PO_4 impregnation of the particles and consequently the development of the pore network in the inner particle [87].

In a recent publication, Cui and Atkinson [89] systematically investigated liquid glycerol AMC using various acid catalysts (i.e. H_2SO_4, H_3PO_4, HCl and CH_3COOH) aiming to study the effect of the acid carbonization conditions onto the textural properties of glycerol-derived nanoporous carbon materials obtained by subsequent physical activation with steam and CO_2. The AMC of glycerol was made under nitrogen between 400 and 800°C, and the highest carbonization yields were obtained at 400°C for 10:3 volumetric mixtures glycerol:acid (30% yield for H_2SO_4 and 50% yield for H_3PO_4). Upon activation, materials with BET area values ranging between 990 and 2470 $m^2 g^{-1}$ and tailored porosity were obtained. The H_3PO_4-char originated micro + mesoporous carbon materials with the volume of mesopores being more than 50% of the total porosity regardless the physical activating agent and the amount of acid during the AMC, while the steam activation of the H_2SO_4-char lead to materials with 40–44% mesopore volume, and the CO_2 activation only 22–25% mesopore volume. The elemental analysis of the nanoporous carbon materials obtained by H_2SO_4 carbonization revealed the presence of 0.35–0.71% of sulfur and the materials carbonized with H_3PO_4 and activated with CO_2 attained even higher heteroatom doping with phosphorus content between 2.04 and 4.34%.

3.2. Other strategies to synthetize nanoporous carbons

3.2.1. Variations of hydrothermal carbonization (HTC) process

In parallel with the studies centered in the activation of hydrochars, in the last few years, the scientific community also started to explore new synthesis routes to obtain a porous structure during the HTC step, being prepared porous carbons with BET surface areas up to 700$m^2 g^{-1}$. The methodologies proposed avoid the need of further thermal or chemical activation, may enable the synthesis of heteroatom-doped solids [90] and can also allow the synthesis of hierarchical materials [91].

Fechler et al. reported the synthesis of porous carbon materials with BET areas between 425 and 672 $m^2 g^{-1}$ through HTC (180°C overnight) of glucose mixed with several eutectic salt mixtures (i.e. $LiCl/ZnCl_2$, $NaCl/ZnCl_2$, and $KCl/ZnCl_2$) in the presence of a small amount of water [90]. The authors proved that both the amount of water added and the salt composition are determinant for the successful synthesis of materials, which are formed by very small particles aggregation, identical to aerogels. The use of the eutectic mixture $LiCl/ZnCl_2$ originated the carbon materials with the highest surface area. When 2-pyrrol-carboxyaldehyde was added as co-reagent of the mixture glucose and $ZnCl_2$, a material with 3% of nitrogen and BET area of 576 $m^2 g^{-1}$ was obtained. Fellinger et al. used glucose as carbon source and borax ($Na_2B_4O_7$) as

both catalyst and structure-directing agent to prepare hierarchical structured carbogels under HTC conditions [91]. Further carbonization under nitrogen at 550 or 1000°C allowed to obtain a carbon material with a BET area of 614 m² g⁻¹ and 70% of mesopore volume.

3.2.2. Carbonization of organic salts

In 2010, Zhou and co-workers developed mesoporous carbons by the carbonization of organic salts (magnesium and barium citrates) evaluating the influence of the temperature of the thermal treatment (600–800°C) [92]. In the case of magnesium salt, BET areas up to 2322 m² g⁻¹ were attained, and the increase of temperature resulted in a progressive increase of the mesopore volume percentage (from 50 to 100%). The barium citrate-derived materials are mainly mesoporous (>90%) and, independently of the temperature, pores between 10 and 20 nm are obtained. Calcium citrate was tested by other authors who reported the paramount importance of temperature in the textural properties of the mesoporous carbons [93].

Atkinson and Rood proposed the use of dichloroacetates of alkaline metals as carbon precursors for the synthesis of nanoporous carbons, being the pore networks, once again, dependent on the cation [94]. The pore structure is produced by fast pyrolysis (15 s to 7 min) under nitrogen flow at temperatures between 300 and 1100°C, and materials attained BET areas of 740 m² g⁻¹. This methodology allowed the synthesis of microporous materials when lithium salt was used and micro + mesoporous solids for the other two metals. In the same research line, Xu and co-workers reported the pyrolysis of EDTA salts to obtain nitrogen-doped porous carbons with BET areas reaching 1800 m² g⁻¹ and porosity characteristics dependent on the thermal treatment temperature (higher the temperature, higher the mesopore volume) [95, 96].

The protocol of organic salts carbonization was extended to gluconates and alginates along with citrates to understand the mechanism of the porosity development [97–99]. The results shown that the textural properties of the porous carbon materials obtained by this methodology are heavily dependent on the type of the cation in the organic salt: while potassium salts originate essentially microporous solids, for sodium and calcium the amount of mesopores is also relevant [98]. In the case of calcium citrate-derived material, the development of the mesoporosity was attributed to the formation of CaO nanoparticles, which act as endotemplates during the carbonization. It was also shown that the nature of the organic salt has a great impact on the morphology, with sodium gluconate leading to the formation of large carbon nanosheets, while sodium citrate originates sponge-like particles. The synthesis of nitrogen-doped porous carbons was also explored by mixing potassium gluconate with melamine, which allowed to obtain a microporous material gathering 22.9% of nitrogen with 660 m² g⁻¹ of BET area [97]. The endotemplate approach on the carbonization of organic salts was further explored with iron, calcium and zinc citrates [99]. The carbonization of these nonalkali organic salts produces mesoporous materials with BET areas between 950 and 1610 m² g⁻¹ and distinct pore size distributions: monomodal distribution centered at 11 nm for calcium citrate, bimodal distribution centered at 9 and 20 nm for iron citrate, and bimodal distribution centered at 3 and 10 nm for iron citrate. These carbons can be post-functionalized by heat treatment in the presence of melamine to obtain materials gathering high BET area and mesopore volume with high nitrogen content (8–9%).

3.2.3. Ionothermal approaches

The synthesis of porous carbon materials *via* ionothermal concept derives from the methodologies proposed in 2004 by Morris and co-workers to prepare zeolite analogues (i.e. inorganic materials) using ionic liquids or eutectic mixtures as both solvents and inorganic structure directing agents (templates) [100]. The ionothermal approach is analogous to hydrothermal and solvothermal processes, where the solvents are predominantly molecular (water or nonaqueous solvents, respectively) but, as the name means, it refers to processes occurring in ionic solvents (e.g. ionic liquids or eutectic mixtures) [100]. The low vapor pressure of the ionic solvents is a great advantage of ionothermal reaction over the hydrothermal or solvothermal concepts, since it allows avoiding the safety concerns connected with the high pressures required to prevent molecular solvent evaporation [101].

The preparation of carbon materials following the ionothermal principles is reported in the literature as both ionothermal and molten salt synthesis processes. Nowadays, there is still not a generally accepted terminology for these processes what turns difficult to understand the classifications and underlying procedures followed by the distinct authors. In fact, the use of ionothermal/molten salt process can be linked either to the preparation of carbon materials with incipient porosity obtained at temperatures ≈ 200°C (ionothermal carbonization—ITC) [102] or to the preparation of porous carbons by a two-step process including the previously mentioned ITC followed by a thermal treatment of the ionothermal derived carbon at high temperatures (attaining 1000°C or more) [103, 104]. Ionothermal/molten salt process is also considered in the case where the mixture of the carbon precursor and the ionic solvent is directly thermally treated at high temperature [105, 106].

The first studies reporting the preparation of porous carbon materials through ionothermal process used ionic liquids as carbon precursors. In 2009, Lee et al. synthesized N-doped materials (2–3%) with BET area values between 640 and 780 $m^2 g^{-1}$, and the authors demonstrated the influence of the ionic liquid nature on the development of mainly microporous or micro + mesoporous materials [107]. In a further work, the authors report a similar process for obtaining materials with up to 17% of nitrogen content, although with lower porosity development [108]. In 2010, other approach of the same research group gathered an ionic liquid with simple carbohydrates allowing to obtain carbon materials with a highly developed mesopore network after treatment at only 200°C during 20 h in a nonpressurized chamber [102]. Xie et al. reported the synthesis of magnetic hierarchical porous carbons by using several carbohydrates and an iron containing ionic liquid, and the authors proposed that the ionic liquid has a triple role: salt template, solvent and catalyst [103].

In the subsequent research in ionothermal approaches (**Table 3**), the introduction of salts as co-reagents became common and generally accepted as a hard template route. Zinc chloride is by far the most frequently reported salt, used alone or in mixtures (eutectic or not) with other salts. This strategy allowed to synthesize porous carbons with ultrahigh surface area (easily around 2000 $m^2 g^{-1}$), hierarchical structure and high heteroatom doping (i.e. nitrogen (>5%) and sulfur). All these features are of fundamental importance for boosting the application of these materials in energy storage processes. Actually, in the great majority of publications, the authors report high performance of the ionothermal-derived porous carbons as supercapacitors. While initially nitrogen-containing ionic liquids were used as carbon precursors [109–111], along the years, the number of studies exploring carbohydrates, or even biomass, as carbon source has increased [105, 106, 112–120].

Reagents	Thermal treatment	BET area (m² g⁻¹)	Observations	Ref.
Imidazolium-based ionic liquids	800 °C (N₂) 1 h	640–780	Micropores or micro + mesopores depending of ionic liquid used 2–3% N-doping	[107]
Imidazolium-based ionic liquids	800 °C (N₂) 1 h	<100	11.4–17.6% N-doping	[108]
Ionic liquid + glucose or fructose	160–200°C, 2–20 h, open air	6–288	Micro + mesopores	[102]
Glucose, fructose, xylose, or starch + iron containing ionic liquid	180°C 24 h	44–155	Hierarchical pores and magnetic	[103]
	Autoclave + 750°C (N₂) 4 h	160–404	Ionic liquid triple role: salt template, solvent, catalyst	
N-containing and N,B-containing ionic liquids + eutectic salt mixtures (alkaline metal and zinc chlorides)	1000°C or 1400°C (N₂)	1100–2000	5% N-doping 6% N + 6% B double doping Pore network dependent on salt mixture and amount	[109]
Glucose, cellulose, or lignin + eutectic salt mixture (KCl/ZnCl₂)	1000°C (N₂) linear or two-step regime	866–2025	V_{Meso}/V_{Total} = 63–92%	[112]
Glucose + molten salt LiCl/KCl + activating oxysalts (KOH, NaBO₂, K₂CO₃, KNO₃, KH₂PO₄, K₂SO₄ or KClO₃)	600–1300°C (N₂)	997–1912	Oxysalt influences morphology V_{Meso}/V_{Total} = 21–52% oxysalt dependent	[113]
Glucose, cellulose, or sugar cane bagasse + metal free ionic liquids	200°C 24 h (autoclave) + 600–900°C (N₂)	16–627	2.8–6.6% N-doping Micro + mesopores	[104]
Peanut shell + salt mixtures (Na₂CO₃/K₂CO₃, Li₂CO₃/Na₂CO₃/K₂CO₃, CaCl₂, CaCl₂/NaCl)	850°C (N₂) 1 h	316–408		[120]
Imidium ionic liquid + eutectic salt mixture (KCl/ZnCl₂)	850°C (N₂) 2 h	1056	2.8% N-doping and 5.16% S-doping	[110]
Imidazolium ionic liquid + salt mixture (NaCl/ZnCl₂)	1000°C (N₂) 2 h	1410–1770	3.7–4.5% N-doping	[111]
Molten ZnCl₂ + common organic solvents (e.g. ethanol, acetonitrile, dimethylsulfoxide, glycerol)	550 °C Schlenck-type reactor	750–1650	14% N-doping or 13% S-doping Aerogel, nanosheet or hyperbranch morphology dependent on solvent	[121]
ZnCl₂ + glucose or glucosamine dissolved in H₂O (+ 2-thiophenecarboxylic acid (TCA))	900–1000°C (N₂)	881–1246	Hierarchical pores N,S-doping (5.6% N and 1.8%S) Carbon aerogels	[122]
Glucose and melamine + eutectic salt mixture (LiCl/KCl)	550–1000°C 5 h (N₂)	387–1190	6–24% N-doping	[106]

Reagents	Thermal treatment	BET area (m² g⁻¹)	Observations	Ref.
Melamine and terephthalaldehyde + salt mixture (KCl/ZnCl₂)	700°C (N₂) 2 h	426–1992		[114]
Glucose, cellulose, lignin (+ melamine) + eutectic salt mixture (KCl/ZnCl₂)	800 °C (N₂) two-step regime	1273–1834	11.9% N-doping V_{Meso}/V_{Total} = 69.2–97.5%	[115]
Glucose + eutectic and noneutectic salt mixture (KCl/ZnCl₂)	350°C 2 h + 900°C 1 h (N₂)	1000–2160	V_{Meso}/V_{Total} > 50%	[105]
Phloroglucinol + glyoxylic acid + pluronic F127 + H₂O + salts (LiCl, NaCl, KCl); pH control	600–900°C (Ar)	535–1815	V_{Meso}/V_{Total} = 15–60%	[123]
Lignin from beech wood + nitration + eutectic salt mixture (KCl/ZnCl₂)	850°C	1381–1589	5.3–6.1% N-doping	[117]
Adenine + eutectic and noneutectic salt mixture (NaCl/ZnCl₂)	900 °C (N₂) 1 h	1770–2900	5.9–7.7% N-doping Pore structure dependent on NaCl proportion (micro + mesopores)	[116]
Tofu + LiCl/KCl + LiNO₃	850°C (Ar) 2 h	1200	1.54–4.72% N-doping Micropores	[119]
Wheat straws + salt mixture (LiCl/KCl) + LiNO₃	650–850°C (N₂) 2 h	1067	4.28% N-doping	[118]

Table 3. Chronological overview of porous carbon synthesis by ionothermal approaches (2009–2017).

More elaborated synthesis schemes have been reported, as is the case of the work developed by Chang et al. [121] where organic solvents were added dropwise to molten $ZnCl_2$ at 550°C. By changing the solvent, the authors were able to obtain nitrogen (14%) or sulfur (13%) doped porous carbons with different morphologies (i.e. aerogel, nanosheets or hyperbranch). There are also reports on ITC of biomass with nitrogen-containing ionic liquid followed by conventional KOH activation to yield nitrogen doping up to 1.59% and apparent surface areas of 2838 m² g⁻¹ [124]. The ionothermal approach is actually a powerful route to synthesize porous carbon materials with valuable graphene-like (2D) structures [125–128].

It is also possible to found reports on highly mesoporous carbon materials obtained by $ZnCl_2$-mediated ionothermal/molten salt synthesis [129–131]. Although these routes are presented as novel synthesis procedures, the high mesopore volumes reported are most probably the result of the complex $ZnCl_2$ activation mechanism when very high amount of $ZnCl_2$ is added. As it was previously mentioned, the behavior of chemical activating agents as templates during carbonization cannot be disregarded, and for the particular case on $ZnCl_2$, the results obtained by Molina-Sabio and Rodríguez-Reinoso [30] allowed the authors to conclude that this chemical acts as template for the creation of porosity. So, although new materials are being produced under "novel" synthesis procedures with appealing names, in some cases, the experimental route and underlying mechanism for pore creation seems to be the one accepted for conventional chemical activation.

For more information regarding the preparation of porous carbon materials *via* ionothermal/molten salt approaches and also their main applications, several review works are available in the literature [132–136].

4. Conclusion

The technological relevance of porous carbon materials continues to prompt the scientific community and companies to explore alternative routes to the conventional methods, in order to develop specialized materials or improve the production process (e.g. optimizing energy costs and minimizing wastes).

The great majority of conventional and innovative processes allowing the synthesis of porous carbons involve heat treatments at moderate-to-high temperatures for carbonization to occur and subsequent formation of the porous carbon skeleton. In the case of chemical activation or ionothermal/molten salt processes, a washing step with water or 10% HCl is required to remove chemical compounds clog the porosity.

Conventional methods are based on a solid and structured carbon material and therefore activation occurs by gasification, selective oxidation of the most reactive carbon atoms and heteroatoms or intercalation processes. Thus, the conventional methodologies are considered top-down processes. Regarding innovative approaches both top-down and bottom-up routes are reported in the literature. HTC or inonothermal reactions promote a top-down process when the carbon precursor is a biomass, but is a bottom-up route when discrete entities (e.g. carbohydrates or ionic liquids) are the starting materials. The acid-mediated degradation of biomass is a top-down route that converts biomass in a carbohydrate-rich acid liquor that is carbonized in a bottom-up approach. Some of the advantages of these novel approaches over the conventional ones are related to the possibility of producing highly porous carbon materials with easier pore size distribution tuning, high amounts of heteroatoms in the surface, and fine control of morphology (e.g. sponge-like, aerogel-like, spherical, sheets (2D)). In light of a more sustainable and circular economy, it is also relevant that some of the novel synthetic approaches (e.g. HTC) allow enabling future large-scale production based on high moisture containing biomass residues and even liquids (e.g. glycerol).

The driving force for the development of new porous carbons throughout these non-conventional methods is the search for high performing materials for electrochemical applications and energy storage, which request hierarchically porous structures ideally doped with electron-rich nonmetallic elements (e.g. nitrogen, sulfur) to increase the conductivity.

The carbon atom is a versatile element that since the Stone Age has reinvented itself. So, the overlook of this chapter allows to predict that in the near future the number of novel synthesis routes to feed the demand for even more specialized porous carbons will continue to increase. This may occur by revisiting synthesis routes established for other classes of materials or by the discovery of completely novel processes.

Acknowledgements

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References

[1] Jäger H, Frohs W, Collin G, von Sturm F, Vohler O, Nutsch G. Carbon, 1. General. Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2010. DOI: 10.1002/14356007.a05_095.pub2

[2] Greenwood NN, Earnshaw A. Chemistry of the Elements. 2nd ed. Butterworth-Heinemann Elsevier: Oxford, UK; 2006

[3] Przepiórski J. Activated carbon filters and their industrial applications. In: Bandosz TJ, editor. Activated Carbon Surfaces in Environmental Remediation. New York: Elsevier; 2006. pp. 421-474. DOI: 10.1016/S1573-4285(06)80018-9

[4] Derbyshire F, Jagtoyen M, Thwaites M. Porosity in Carbons. London: Edward Arnold; 1995

[5] Çeçen F. Activated carbon. In: Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.; 2014. pp. 1-34. DOI: 10.1002/0471238961.0103200902011105.a01.pub3

[6] Çeçen F. Water and wastewater treatment: Historical perspective of activated carbon adsorption and its integration with biological processes. In: Çeçen F, Aktaş Ö, editors. Activated Carbon for Water and Wastewater Treatment. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2011. pp. 1-11. DOI: 10.1002/9783527639441.ch1

[7] Dąbrowski A. Adsorption—From theory to practice. Advances in Colloid and Interface Science. 2001;**93**(1-3):135-224. DOI: 10.1016/S0001-8686(00)00082-8

[8] Menéndez-Diaz JÁ, Martín-Gullón I. Types of carbon adsorbents and their production. In: Bandosz TJ, editor. Activated Carbon Surfaces in Environmental Remediation. New York: Elsevier; 2006. pp. 1-48. DOI: 10.1016/S1573-4285(06)80010-4

[9] University of Kentucky, Center for Applied Energy Research, web information; Available from: "http://www.caer.uky.edu/carbon/history/carbonhistory.shtml" (Accessed: 2017-05-15)

[10] Ostrejko R. (British Patent 14,224, 1900; French Patent 304,867, 1901; German Patent 136,792, 1901; US Patent 739,104) 1903. Available from: http://speicyte.wix.com/raphael-von-ostrejko [Accessed: 2017-07-05]

[11] Bandosz TJ. Nanoporous carbons: Looking beyond their perception as adsorbents, catalyst supports and Supercapacitors. The Chemical Record. 2016;**16**(1):205-218. DOI: 10.1002/tcr.201500231

[12] Rodríguez-Reinoso F, Sepúlveda-Escribano A. Porous carbons in adsorption and catalysis. In: Nalwa HS, editor. Handbook of Surfaces and Interfaces of Materials. San Diego: Academic Press; 2001. pp. 309-355

[13] Rodríguez-Reinoso F, Seúlveda-Escribano A. Carbon as Catalyst Support. Carbon Materials for Catalysis. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2008. pp. 131-155. DOI: 10.1002/9780470403709.ch4

[14] Figueiredo JL, Pereira MFR. Carbon as Catalyst. Carbon Materials for Catalysis. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2008. pp. 177-217. DOI: 10.1002/9780470403709.ch6

[15] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C60: Buckminsterfullerene. Nature. 1985;**318**(6042):162-163. DOI: 10.1038/318162a0

[16] Iijima S. Helical microtubules of graphitic carbon. Nature. 1991;**354**(6348):56-58. DOI: 10.1038/354056a0

[17] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. Science. 2004;**306**(5696):666-669. DOI: 10.1126/science.1102896

[18] Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, Sing KSW. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). Pure and Applied Chemistry. 2015;**87**(9-10):1051-1069. DOI: 10.1515/pac-2014-1117

[19] Gregg SJ, Sing KSW. Adsorption, Surface Area and Porosity. 2nd ed. London: Academic Press Inc.; 1982. DOI: 10.1002/bbpc.19820861019

[20] Sing KSW, Rouquerol F, Llewellyn P, Rouquerol J. 9—Assessment of microporosity. In: Adsorption by Powders and Porous Solids. 2nd ed. Oxford: Academic Press; 2014. pp. 303-320. DOI: 10.1016/B978-0-08-097035-6.00009-7

[21] Choma J, Jaroniec M. Characterization of nanoporous carbons by using gas adsorption isotherms. In: Bandosz TJ, editor. Activated Carbon Surfaces in Environmental Remediation. New York: Elsevier; 2006. pp. 107-158. DOI: 10.1016/S1573-4285(06)80012-8

[22] KSW S. 10—Adsorption by active carbons. In: Adsorption by Powders and Porous Solids. 2nd ed. Oxford: Academic Press; 2014. pp. 321-391. DOI: 10.1016/B978-0-08-097035-6.00010-3

[23] Bandosz TJ, Ania CO. Surface chemistry of activated carbons and its characterization. In: Bandosz TJ, editor. Activated Carbon Surfaces in Environmental Remediation. New York: Elsevier; 2006. pp. 159-229. DOI: 10.1016/S1573-4285(06)80013-X

[24] Marsh H, Rodríguez-Reinoso F. Activated Carbon. Oxford: Elsevier; 2006

[25] Bansal RC, Donnet J-B, Stoeckli R. Active Carbon. New York: Marcel Dekker; 1988

[26] Bandosz TJ. Activated Carbon Surfaces in Environmental Remediation. 1st ed. New York: Elsevier Ltd; 2006

[27] Bottani EJ, Tascón JMD. Adsorption by Carbons. Oxford: Elsevier Ltd.; 2008

[28] Hu Z, Vansant EF. Synthesis and characterization of a controlled-micropore-size carbonaceous adsorbent produced from walnut shell. Microporous Materials. 1995;**3**(6):603-612. DOI: 10.1016/0927-6513(94)00067-6

[29] Wang J, Kaskel S. KOH activation of carbon-based materials for energy storage. Journal of Materials Chemistry. 2012;**22**(45):23710-23725. DOI: 10.1039/C2JM34066F

[30] Molina-Sabio M, Rodríguez-Reinoso F. Role of chemical activation in the development of carbon porosity. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2004;**241**(1):15-25. DOI: 10.1016/j.colsurfa.2004.04.007

[31] Lota G, Centeno TA, Frackowiak E, Stoeckli F. Improvement of the structural and chemical properties of a commercial activated carbon for its application in electrochemical capacitors. Electrochimica Acta. 2008;**53**(5):2210-2216. DOI: 10.1016/j.electacta.2007.09.028

[32] Kunowsky M, Marco-Lozar JP, Cazorla-Amorós D, Linares-Solano A. Scale-up activation of carbon fibres for hydrogen storage. International Journal of Hydrogen Energy. 2010;**35**(6):2393-2402. DOI: 10.1016/j.ijhydene.2009.12.151

[33] Wang J, Yang X, Wu D, Fu R, Dresselhaus MS, Dresselhaus G. The porous structures of activated carbon aerogels and their effects on electrochemical performance. Journal of Power Sources. 2008;**185**(1):589-594. DOI: 10.1016/j.jpowsour.2008.06.070

[34] Mestre AS, Freire C, Pires J, Carvalho AP, Pinto ML. High performance microspherical activated carbons for methane storage and landfill gas or biogas upgrade. Journal of Materials Chemistry A. 2014;**2**(37):15337-15344. DOI: 10.1039/C4TA03242J

[35] Mestre AS, Tyszko E, Andrade MA, Galhetas M, Freire C, Carvalho AP. Sustainable activated carbons prepared from a sucrose-derived hydrochar: Remarkable adsorbents for pharmaceutical compounds. RSC Advances. 2015;**5**(25):19696-19707. DOI: 10.1039/C4RA14495C

[36] Mestre AS, Pires J, Nogueira JMF, Carvalho AP. Activated carbons for the adsorption of ibuprofen. Carbon. 2007;**45**(10):1979-1988. DOI: 10.1016/j.carbon.2007.06.005

[37] Enterria M, Figueiredo JL. Nanostructured mesoporous carbons: Tuning texture and surface chemistry. Carbon. 2016;**108**:79-102. DOI: 10.1016/j.carbon.2016.06.108

[38] Lee J, Kim J, Hyeon T. Recent progress in the synthesis of porous carbon materials. Advanced Materials. 2006;**18**(16):2073-2094. DOI: 10.1002/adma.200501576

[39] Ma TY, Liu L, Yuan ZY. Direct synthesis of ordered mesoporous carbons. Chemical Society Reviews. 2013;**42**(9):3977-4003. DOI: 10.1039/c2cs35301f

[40] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde. Journal of Materials Science. 1989;**24**(9):3221-3227. DOI: 10.1007/bf01139044

[41] ElKhatat AM, Al-Muhtaseb SA. Advances in tailoring resorcinol-formaldehyde organic and carbon gels. Advanced Materials. 2011;**23**(26):2887-2903. DOI: 10.1002/adma.201100283

[42] Tamon H, Ishizaka H, Yamamoto T, Suzuki T. Preparation of mesoporous carbon by freeze drying. Carbon. 1999;**37**(12):2049-2055. DOI: 10.1016/S0008-6223(99)00089-5

[43] Rasines G, Macias C, Haro M, Jagiello J, Ania CO. Effects of CO_2 activation of carbon aerogels leading to ultrahigh micro-meso porosity. Microporous Mesoporous Materials. 2015;**209**:18-22. DOI: 10.1016/j.micromeso.2015.01.011

[44] Fairén-Jiménez D, Carrasco-Marín F, Moreno-Castilla C. Porosity and surface area of monolithic carbon aerogels prepared using alkaline carbonates and organic acids as polymerization catalysts. Carbon. 2006;**44**(11):2301-2307. DOI: 10.1016/j.carbon.2006.02.021

[45] Gomis-Berenguer A, García-González R, Mestre AS, Ania CO. Designing micro- and mesoporous carbon networks by chemical activation of organic resins. Adsorption. 2017;**23**(2):303-312. DOI: 10.1007/s10450-016-9851-4

[46] Al-Muhtaseb SA, Ritter JA. Preparation and properties of resorcinol-formaldehyde organic and carbon gels. Advanced Materials. 2003;**15**(2):101-114. DOI: 10.1002/adma.200390020

[47] James LK. Nobel Laureates in Chemistry, 1901-1992 (History of Modern Chemical Sciences). 1st ed. American Chemical Society and the Chemical Heritage Foundation; 1993

[48] Marinovic A, Pileidis FD, Titirici M-M. Chapter 5. Hydrothermal Carbonisation (HTC): History, State-of-the-Art and Chemistry. Porous Carbon Materials from Sustainable Precursors. The Royal Society of Chemistry; 2015. pp. 129-55. DOI: 10.1039/9781782622277-00129

[49] Sevilla M, Fuertes AB. Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. Chemistry—A European Journal. 2009;**15**(16):4195-4203. DOI: 10.1002/chem.200802097

[50] Wang Q, Li H, Chen L, Huang X. Monodispersed hard carbon spherules with uniform nanopores. Carbon. 2001;**39**(14):2211-2214. DOI: 10.1016/s0008-6223(01)00040-9

[51] Zhao L, Fan LZ, Zhou MQ, Guan H, Qiao SY, Antonietti M, Titirici MM. Nitrogen-containing hydrothermal carbons with superior performance in supercapacitors. Advanced Materials. 2010;**22**(45):5202-5206. DOI: 10.1002/adma.201002647

[52] Jain A, Jayaraman S, Balasubramanian R, Srinivasan MP. Hydrothermal pre-treatment for mesoporous carbon synthesis: Enhancement of chemical activation. Journal of Materials Chemistry A. 2014;**2**(2):520-528. DOI: 10.1039/C3TA12648J

[53] Liu TT, Li Y, Peng NN, Lang QQ, Xia Y, Gai C, Zheng QF, Liu ZG. Heteroatoms doped porous carbon derived from hydrothermally treated sewage sludge: Structural characterization and environmental application. Journal of Environmental Management. 2017;**197**:151-158. DOI: 10.1016/j.jenvman.2017.03.082

[54] Zhao YQ, Lu M, Tao PY, Zhang YJ, Gong XT, Yang Z, Zhang GQ, Li HL. Hierarchically porous and heteroatom doped carbon derived from tobacco rods for supercapacitors. Journal of Power Sources. 2016;**307**:391-400. DOI: 10.1016/j.jpowsour.2016.01.020

[55] Islam MA, Ahmed MJ, Khanday WA, Asif M, Hameed BH. Mesoporous activated carbon prepared from NaOH activation of rattan (Lacosperma secundiflorum) hydrochar for methylene blue removal. Ecotoxicology and Environmental Safety. 2017;**138**:279-285. DOI: 10.1016/j.ecoenv.2017.01.010

[56] Fuertes AB, Sevilla M. High-surface area carbons from renewable sources with a bimodal micro-mesoporosity for high-performance ionic liquid-based supercapacitors. Carbon. 2015;**94**:41-52. DOI: 10.1016/j.carbon.2015.06.028

[57] Chen XF, Zhang JY, Zhang B, Dong SM, Guo XC, Mu XD, Fei BH. A novel hierarchical porous nitrogen-doped carbon derived from bamboo shoot for high performance supercapacitor. Scientific Reports. 2017;**7**:7362-7372. DOI: 10.1038/s41598-017-06730-x

[58] Falco C, Marco-Lozar JP, Salinas-Torres D, Morallón E, Cazorla-Amorós D, Titirici MM, Lozano-Castelló D. Tailoring the porosity of chemically activated hydrothermal carbons: Influence of the precursor and hydrothermal carbonization temperature. Carbon. 2013;**62**(0):346-355. DOI: 10.1016/j.carbon.2013.06.017

[59] Li M, Li W, Liu S. Hydrothermal synthesis, characterization, and KOH activation of carbon spheres from glucose. Carbohydrate Research. 2011;**346**(8):999-1004. DOI: 10.1016/j.carres.2011.03.020

[60] Romero-Anaya AJ, Ouzzine M, Lillo-Ródenas MA, Linares-Solano A. Spherical carbons: Synthesis, characterization and activation processes. Carbon. 2014;**68**(0):296-307. DOI: 10.1016/j.carbon.2013.11.006

[61] He CL, Liu YL, Xue ZP, Zheng MT, Wang HB, Xiao Y, Dong HW, Zhang HR, Lei BF. Simple synthesis of carboxylate-rich porous carbon microspheres for high-performance supercapacitor electrode materials. International Journal of Electrochemical Science. 2013;**8**(5):7088-7098

[62] Yuan B, Wang J, Chen Y, Wu X, Luo H, Deng S. Unprecedented performance of N-doped activated hydrothermal carbon towards C_2H_6/CH_4, CO_2/CH_4, and CO_2/H_2 separation. Journal of Materials Chemistry A. 2016;**4**(6):2263-2276. DOI: 10.1039/C5TA08436A

[63] Sevilla M, Falco C, Titirici MM, Fuertes AB. High-performance CO_2 sorbents from algae. RSC Advances. 2012;**2**(33):12792-12797. DOI: 10.1039/C2ra22552b

[64] White RJ, Yoshizawa N, Antonietti M, Titirici MM. A sustainable synthesis of nitrogen-doped carbon aerogels. Green Chemistry. 2011;**13**(9):2428-2434. DOI: 10.1039/c1gc15349h

[65] Sevilla M, Ferrero GA, Fuertes AB. Beyond KOH activation for the synthesis of superactivated carbons from hydrochar. Carbon. 2017;**114**:50-58. DOI: 10.1016/j.carbon.2016.12.010

[66] Fang J, Zhan L, Ok YS, Gao B. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. Journal of Industrial and Engineering Chemistry. 2018;**57**:15-21. DOI: 10.1016/j.jiec.2017.08.026

[67] Jain A, Balasubramanian R, Srinivasan MP. Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review. Chemical Engineering Journal. 2016;**283**:789-805. DOI: 10.1016/j.cej.2015.08.014

[68] Zhu X, Liu Y, Qian F, Zhou C, Zhang S, Chen J. Role of hydrochar properties on the porosity of hydrochar-based porous carbon for their sustainable application. ACS Sustainable Chemistry & Engineering. 2015;**3**(5):833-840. DOI: 10.1021/acssuschemeng.5b00153

[69] Chen RF, Li LQ, Liu Z, Lu MM, Wang CH, Li HL, Ma WW, Wang SB. Preparation and characterization of activated carbons from tobacco stem by chemical activation. Journal of the Air & Waste Management Association. 2017;**67**(6):713-724. DOI: 10.1080/10962247.2017.1280560

[70] Adebisi GA, Chowdhury ZZ, Abd Hamid SB, Ali E. Equilibrium isotherm, kinetic, and thermodynamic studies of divalent cation adsorption onto Calamus gracilis sawdust-based activated carbon. BioResources. 2017;**12**(2):2872-2898. DOI: 10.15376/biores.12.2.2872-2898

[71] Sevilla M, Fuertes AB. Sustainable porous carbons with a superior performance for CO_2 capture. Energy & Environmental Science. 2011;**4**(5):1765-1771. DOI: 10.1039/C0ee00784f

[72] Sevilla M, Fuertes AB, Mokaya R. High density hydrogen storage in superactivated carbons from hydrothermally carbonized renewable organic materials. Energy & Environmental Science. 2011;**4**(4):1400-1410. DOI: 10.1039/C0ee00347f

[73] Wei L, Sevilla M, Fuertes AB, Mokaya R, Yushin G. Hydrothermal carbonization of abundant renewable natural organic chemicals for high-performance supercapacitor electrodes. Advanced Energy Materials. 2011;**1**(3):356-361. DOI: 10.1002/aenm.201100019

[74] Falco C, Sieben JM, Brun N, Sevilla M, van der Mauelen T, Morallon E, Cazorla-Amorós D, Titirici MM. Hydrothermal carbons from hemicellulose-derived aqueous hydrolysis products as electrode materials for supercapacitors. ChemSusChem 2013;**6**(2):374-382. DOI: 10.1002/cssc.201200817

[75] Unur E. Functional nanoporous carbons from hydrothermally treated biomass for environmental purification. Microporous and Mesoporous Materials. 2013;**168**(0):92-101. DOI: 10.1016/j.micromeso.2012.09.027

[76] Wang HL, Li Z, Tak JK, Holt CMB, Tan XH, Xu ZW, Amirkhiz BS, Hayfield D, Anyia A, Stephenson T, Mitlin D. Supercapacitors based on carbons with tuned porosity derived from paper pulp mill sludge biowaste. Carbon. 2013;**57**:317-328. DOI: 10.1016/j.carbon.2013.01.079

[77] Coromina HM, Walsh DA, Mokaya R. Biomass-derived activated carbon with simultaneously enhanced CO_2 uptake for both pre and post combustion capture applications. Journal of Materials Chemistry A. 2016;**4**(1):280-289. DOI: 10.1039/C5TA09202G

[78] Feng HB, Hu H, Dong HW, Xiao Y, Cai YJ, Lei BF, Liu YL, Zheng MT. Hierarchical structured carbon derived from bagasse wastes: A simple and efficient synthesis route and its improved electrochemical properties for high-performance supercapacitors. Journal of Power Sources. 2016;**302**:164-173. DOI: 10.1016/j.jpowsour.2015.10.063

[79] Hao S-W, Hsu C-H, Liu Y-G, Chang BK. Activated carbon derived from hydrothermal treatment of sucrose and its air filtration application. RSC Advances. 2016;**6**(111):109950-109959. DOI: 10.1039/C6RA23958G

[80] Bedin KC, Martins AC, Cazetta AL, Pezoti O, Almeida VC. KOH-activated carbon prepared from sucrose spherical carbon: Adsorption equilibrium, kinetic and thermodynamic studies for methylene blue removal. Chemical Engineering Journal. 2016;**286**:476-484. DOI: 10.1016/j.cej.2015.10.099

[81] Balahmar N, Al-Jumialy AS, Mokaya R. Biomass to porous carbon in one step: Directly activated biomass for high performance CO_2 storage. Journal of Materials Chemistry A. 2017;**5**(24):12330-12339. DOI: 10.1039/c7ta01722g

[82] Islam MA, Tan IAW, Benhouria A, Asif M, Hameed BH. Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation. Chemical Engineering Journal. 2015;**270**:187-195. DOI: 10.1016/j.cej.2015.01.058

[83] Tran HN, You SJ, Chao HP. Fast and efficient adsorption of methylene green 5 on activated carbon prepared from new chemical activation method. Journal of Environmental Management. 2017;**188**:322-336. DOI: 10.1016/j.jenvman.2016.12.003

[84] Liu Z, Zhang F-S. Removal of copper(II) and phenol from aqueous solution using porous carbons derived from hydrothermal chars. Desalination. 2011;**267**(1):101-106. DOI: 10.1016/j.desal.2010.09.013

[85] Román S, Valente Nabais JM, Ledesma B, González JF, Laginhas C, Titirici MM. Production of low-cost adsorbents with tunable surface chemistry by conjunction of hydrothermal carbonization and activation processes. Microporous and Mesoporous Materials. 2013;**165**(0):127-133. DOI: 10.1016/j.micromeso.2012.08.006

[86] Harmer MA, Fan A, Liauw A, Kumar RK. A new route to high yield sugars from biomass: Phosphoric-sulfuric acid. Chemical Communications. 2009;(43):6610-6612. DOI: 10.1039/B916048E

[87] Wang L, Guo Y, Zou B, Rong C, Ma X, Qu Y, Li Y, Wang Z. High surface area porous carbons prepared from hydrochars by phosphoric acid activation. Bioresource Technology. 2011;**102**(2):1947-1950. DOI: 10.1016/j.biortech.2010.08.100

[88] Wang L, Guo Y, Zhu Y, Li Y, Qu Y, Rong C, Ma X, Wang Z. A new route for preparation of hydrochars from rice husk. Bioresource Technology. 2010;**101**(24):9807-9810. DOI: 10.1016/j.biortech.2010.07.031

[89] Cui Y, Atkinson JD. Tailored activated carbon from glycerol: Role of acid dehydrator on physiochemical characteristics and adsorption performance. Journal of Materials Chemistry A. 2017;**5**(32):16812-16821. DOI: 10.1039/C7TA02898A

[90] Fechler N, Wohlgemuth S-A, Jaker P, Antonietti M. Salt and sugar: Direct synthesis of high surface area carbon materials at low temperatures via hydrothermal carbonization of glucose under hypersaline conditions. Journal of Materials Chemistry A. 2013;**1**(33):9418-9421. DOI: 10.1039/C3TA10674H

[91] Fellinger TP, White RJ, Titirici MM, Antonietti M. Borax-mediated formation of carbon aerogels from glucose. Advanced Functional Materials. 2012;**22**(15):3254-3260. DOI: 10.1002/adfm.201102920

[92] Zhou J, Yuan X, Xing W, Si WJ, Zhuo SP. Capacitive performance of mesoporous carbons derived from the citrates in ionic liquid. Carbon. 2010;**48**(10):2765-2772. DOI: 10.1016/j.carbon.2010.04.004

[93] Zhou QQ, Chen XY, Wang B. An activation-free protocol for preparing porous carbon from calcium citrate and the capacitive performance. Microporous Mesoporous Materials. 2012;**158**:155-161. DOI: 10.1016/j.micromeso.2012.03.031

[94] Atkinson JD, Rood MJ. Preparing microporous carbon from solid organic salt precursors using in situ templating and a fixed-bed reactor. Microporous Mesoporous Materials. 2012;**160**:174-181. DOI: 10.1016/j.micromeso.2012.05.008

[95] Xu B, Duan H, Chu M, Cao GP, Yang YS. Facile synthesis of nitrogen-doped porous carbon for supercapacitors. Journal of Materials Chemistry A. 2013;**1**(14):4565-4570. DOI: 10.1039/c3ta01637d

[96] Xu B, Zheng DF, Jia MQ, Cao GP, Yang YS. Nitrogen-doped porous carbon simply prepared by pyrolyzing a nitrogen-containing organic salt for supercapacitors. Electrochimica Acta. 2013;**98**:176-182. DOI: 10.1016/j.electacta.2013.03.053

[97] Fuertes AB, Ferrero GA, Sevilla M. One-pot synthesis of microporous carbons highly enriched in nitrogen and their electrochemical performance. Journal of Materials Chemistry A. 2014;**2**(35):14439-14448. DOI: 10.1039/c4ta02959c

[98] Sevilla M, Fuertes AB. A general and facile synthesis strategy towards highly porous carbons: Carbonization of organic salts. Journal of Materials Chemistry A. 2013;**1**(44):13738-13741. DOI: 10.1039/c3ta13149a

[99] Ferrero GA, Sevilla M, Fuertes AB. Mesoporous carbons synthesized by direct carbonization of citrate salts for use as high-performance capacitors. Carbon. 2015;**88**:239-251. DOI: 10.1016/j.carbon.2015.03.014

[100] Cooper ER, Andrews CD, Wheatley PS, Webb PB, Wormald P, Morris RE. Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. Nature. 2004;**430**(7003):1012-1016. DOI: 10.1038/nature02860

[101] Taubert A, Li Z. Inorganic materials from ionic liquids. Dalton Transactions. 2007;(7):723-727. DOI: 10.1039/B616593A

[102] Lee JS, Mayes RT, Luo HM, Dai S. Ionothermal carbonization of sugars in a protic ionic liquid under ambient conditions. Carbon. 2010;**48**(12):3364-3368. DOI: 10.1016/j.carbon.2010.05.027

[103] Xie ZL, White RJ, Weber J, Taubert A, Titirici MM. Hierarchical porous carbonaceous materials via ionothermal carbonization of carbohydrates. Journal of Materials Chemistry. 2011;**21**(20):7434-7442. DOI: 10.1039/c1jm00013f

[104] Zhang PF, Gong YT, Wei ZZ, Wang J, Zhang ZY, Li HR, Dai S, Wang Y. Updating biomass into functional carbon material in ionothermal manner. ACS Applied Materials & Interfaces. 2014;**6**(15):12515-12522. DOI: 10.1021/am5023682

[105] Pampel J, Denton C, Fellinger T-P. Glucose derived ionothermal carbons with tailor-made porosity. Carbon. 2016;**107**:288-296. DOI: 10.1016/j.carbon.2016.06.009

[106] Yu ZF, Wang XZ, Song XD, Liu Y, Qiu JS. Molten salt synthesis of nitrogen-doped porous carbons for hydrogen sulfide adsorptive removal. Carbon. 2015;**95**:852-860. DOI: 10.1016/j.carbon.2015.08.105

[107] Lee JS, Wang XQ, Luo HM, Baker GA, Dai S. Facile ionothermal synthesis of microporous and mesoporous carbons from task specific ionic liquids. Journal of the American Chemical Society. 2009;**131**(13):4596-4597. DOI: 10.1021/ja900686d

[108] Lee JS, Wang XQ, Luo HM, Dai S. Fluidic carbon precursors for formation of functional carbon under ambient pressure based on ionic liquids. Advanced Materials. 2010;**22**(9):1004-1007. DOI: 10.1002/adma.200903403

[109] Fechler N, Fellinger T-P, Antonietti M. "Salt templating": A simple and sustainable pathway toward highly porous functional carbons from ionic liquids. Advanced Materials. 2013;**25**(1):75-79. DOI: 10.1002/adma.201203422

[110] Cui ZT, Wang SG, Zhang YH, Cao MH. A simple and green pathway toward nitrogen and sulfur dual doped hierarchically porous carbons from ionic liquids for oxygen reduction. Journal of Power Sources. 2014;**259**:138-144. DOI: 10.1016/j.jpowsour.2014.02.084

[111] Elumeeva K, Fechler N, Fellinger TP, Antonietti M. Metal-free ionic liquid-derived electrocatalyst for high-performance oxygen reduction in acidic and alkaline electrolytes. Materials Horizons. 2014;**1**(6):588-594. DOI: 10.1039/c4mh00123k

[112] Ma Z, Zhang H, Yang Z, Zhang Y, Yu B, Liu Z. Highly mesoporous carbons derived from biomass feedstocks templated with eutectic salt $ZnCl_2$/KCl. Journal of Materials Chemistry A. 2014;**2**(45):19324-19329. DOI: 10.1039/C4TA03829K

[113] Liu XF, Antonietti M. Molten salt activation for synthesis of porous carbon nanostructures and carbon sheets. Carbon. 2014;**69**:460-466. DOI: 10.1016/j.carbon.2013.12.049

[114] Su SJ, Lai QX, Liang YY. Schiff-base polymer derived nitrogen-rich microporous carbon spheres synthesized by molten-salt route for high-performance supercapacitors. RSC Advances. 2015;**5**(75):60956-60561. DOI: 10.1039/c5ra07628e

[115] Ma Z, Zhang H, Yang Z, Ji G, Yu B, Liu X, Liu Z. Mesoporous nitrogen-doped carbons with high nitrogen contents and ultrahigh surface areas: Synthesis and applications in catalysis. Green Chemistry. 2016;**18**(7):1976-1982. DOI: 10.1039/C5GC01920F

[116] Pampel J, Fellinger TP. Opening of bottleneck pores for the improvement of nitrogen doped carbon electrocatalysts. Advanced Energy Materials. 2016;**6**(8):6-13. DOI: 10.1002/Aenm.201502389

[117] Graglia M, Pampel J, Hantke T, Fellinger TP, Esposito D. Nitro lignin-derived nitrogen-doped carbon as an efficient and sustainable electrocatalyst for oxygen reduction. ACS Nano. 2016;**10**(4):4364-4371. DOI: 10.1021/acsnano.5b08040

[118] Yang F, Sun LL, Xie WL, Jiang Q, Gao Y, Zhang W, Zhang Y. Nitrogen-functionalization biochars derived from wheat straws via molten salt synthesis: An efficient adsorbent for atrazine removal. Science of the Total Environment. 2017;**607**:1391-1399. DOI: 10.1016/j.scitotenv.2017.07.020

[119] Ouyang T, Cheng K, Gao YY, Kong SY, Ye K, Wang GL, Cao DX. Molten salt synthesis of nitrogen doped porous carbon: A new preparation methodology for high-volumetric capacitance electrode materials. Journal of Materials Chemistry A. 2016;**4**(25):9832-9843. DOI: 10.1039/c6ta02673g

[120] Yin H, Lu B, Xu Y, Tang D, Mao X, Xiao W, Wang D, Alshawabkeh AN. Harvesting capacitive carbon by carbonization of waste biomass in molten salts. Environmental Science & Technology. 2014;**48**(14):8101-8108. DOI: 10.1021/es501739v

[121] Chang YQ, Antonietti M, Fellinger TP. Synthesis of nanostructured carbon through Ionothermal carbonization of common organic solvents and solutions. Angewandte Chemie-International Edition. 2015;**54**(18):5507-5512. DOI: 10.1002/anie.201411685

[122] Schipper F, Vizintin A, Ren J, Dominko R, Fellinger T-P. Biomass-derived heteroatom-doped carbon aerogels from a salt melt sol–gel synthesis and their performance in Li–S batteries. ChemSusChem. 2015;**8**(18):3077-3083. DOI: 10.1002/cssc.201500832

[123] Nita C, Bensafia M, Vaulot C, Delmotte L, Matei Ghimbeu C. Insights on the synthesis mechanism of green phenolic resin derived porous carbons via a salt-soft templating approach. Carbon. 2016;**109**:227-238. DOI: 10.1016/j.carbon.2016.08.011

[124] Liu YC, Huang BB, Lin XX, Xie ZL. Biomass-derived hierarchical porous carbons: Boosting the energy density of supercapacitors via an ionothermal approach. Journal of Materials Chemistry A. 2017;**5**(25):13009-13018. DOI: 10.1039/c7ta03639f

[125] Liu XF, Antonietti M. Moderating black powder chemistry for the synthesis of doped and highly porous graphene nanoplatelets and their use in electrocatalysis. Advanced Materials. 2013;**25**(43):6284-6290. DOI: 10.1002/adma.201302034

[126] Liu XF, Giordano C, Antonietti M. A facile molten-salt route to graphene synthesis. Small. 2014;**10**(1):193-200. DOI: 10.1002/smll.201300812

[127] Zhang PF, Qiao ZA, Zhang ZY, Wan S, Dai S. Mesoporous graphene-like carbon sheet: High-power supercapacitor and outstanding catalyst support. Journal of Materials Chemistry A. 2014;**2**(31):12262-12269. DOI: 10.1039/c4ta02307b

[128] He B, Li WC, Lu AH. High nitrogen-content carbon nanosheets formed using the Schiff-base reaction in a molten salt medium as efficient anode materials for lithium-ion batteries. Journal of Materials Chemistry A. 2015;**3**(2):579-585. DOI: 10.1039/c4ta05056h

[129] Deng X, Zhao BT, Zhu L, Shao ZP. Molten salt synthesis of nitrogen-doped carbon with hierarchical pore structures for use as high-performance electrodes in supercapacitors. Carbon. 2015;**93**:48-58. DOI: 10.1016/j.carbon.2015.05.031

[130] Shang HS, Lu YJ, Zhao F, Chao C, Zhang B, Zhang HS. Preparing high surface area porous carbon from biomass by carbonization in a molten salt medium. RSC Advances. 2015;**5**(92):75728-75734. DOI: 10.1039/c5ra12406a

[131] Kong WX, Zhao F, Guan HJ, Zhao YF, Zhang HS, Zhang B. Highly adsorptive mesoporous carbon from biomass using molten-salt route. Journal of Materials Science. 2016;**51**(14): 6793-6800. DOI: 10.1007/s10853-016-9966-8

[132] Fellinger TP, Thomas A, Yuan JY, Antonietti M. 25th anniversary article: "cooking carbon with salt": Carbon materials and carbonaceous frameworks from ionic liquids and poly(ionic liquid)s. Advanced Materials. 2013;**25**(41):5838-5854. DOI: 10.1002/adma.201301975

[133] Antonietti M, Fechler N, Fellinger TP. Carbon aerogels and monoliths: Control of porosity and nanoarchitecture via sol-gel routes. Chemistry of Materials. 2014;**26**(1):196-210. DOI: 10.1021/cm402239e

[134] Liu XF, Fechler N, Antonietti M. Salt melt synthesis of ceramics, semiconductors and carbon nanostructures. Chemical Society Reviews. 2013;**42**(21):8237-8265. DOI: 10.1039/c3cs60159e

[135] Xie ZL, Su DS. Ionic liquid based approaches to carbon materials synthesis. European Journal of Inorganic Chemistry. 2015;(7):1137-1147. DOI: 10.1002/ejic.201402607

[136] Deng YF, Xie Y, Zou KX, Ji XL. Review on recent advances in nitrogen-doped carbons: Preparations and applications in supercapacitors. Journal of Materials Chemistry A. 2016;**4**(4):1144-1173. DOI: 10.1039/c5ta08620e