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Chapter

Nanoporous Carbon Materials toward Phenolic Compounds Adsorption

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Abstract

Nanoporous carbon-based sorbents are used to generate a three-dimensional real-space model of the nanoporous structure using the concept of Gaussian random fields. This pore model is used to derive important pore size characteristics, which are cross-validated against the corresponding values from gas sorption analysis. After filling the model pore structure with an aqueous electrolyte and rearranging the ions via a Monte Carlo simulation for different applied adsorption potentials. In comparison to nanopores formed from solid-state membranes (e.g., silicon oxide, aluminum oxide, polymer membranes, glass, hafnium oxide, gold, etc.) and very recently 2D materials (e.g., boron nitride, molybdenum disulfide, etc.), those nanopores produced from carbon materials (e.g., graphene, carbon nanotubes (CNTs), diamond, etc.), especially those from graphene appear to be perfect for adsorption process. The thickness of carbon structures nanopores can be as thin as 0.35 nm, resembling the height of the base spacing. Moreover, the sizes of carbon structures nanopores can be precisely fabricated and tuned to around 1.0 nm, the similar size of many heavy metals and organic pollutants molecules. Furthermore, carbon materials are chemically stable and feature-rich surface chemistry. Therefore, various carbon nanopore sequencing techniques have been developed. Finally, in this chapter the adsorption of phenolic compounds on nanoporous carbon specifically the active carbon are overviewed and how to affect the heterogeneity of activated carbon surface, PH of the solution on the efficiency of adsorption.

Keywords: nanoporous carbon, phenolic compounds, adsorption, activation process, templating methods

1. Introduction

Contamination of water is one of the significant issues in the universe, that poses negative effects on individual and surroundings. The rising in industrial and human activities resulted in increasing the flowing of wastewater into water supplies [1, 2]. In the last years, the impacts of exposure of human and animals to chemicals in the ambiance especially the aquatics medium has taken the high interest of many scientists and decision-makers [3]. Among these chemicals, phenolic compounds are considered the most important due to their toxic effect on animals and humans.
that result from their staying in the ambient for a long time and then collect to cause
that effect [3]. There are two types of phenolic compounds, natural compounds
connected to the flowers and fruits colors and synthetic compounds used in daily
humans life for various purposes [3]. Phenolic compounds are present in the efflu-
ents of various industries such as oil refining, petrochemicals, pharmaceuticals,
cooking operations, resin manufacturing, plastics, paint, pulp, paper, and wood
products. Discharge of these compounds without treatment may lead to serious
health risks to humans, animals, and aquatic systems [4]. The presence of these
compounds is attributed to a breakdown of natural organic materials in the water,
flows water away from farmland, and discharge of wastes resulting from industries
and humans uses in water resources. The presence of these compounds in water
results in the interaction of them with chemical, physical and biological variables
inside the water that led to their conversion to other forms that have a dangerous
effect than the original ones [3, 5, 6]. Phenol has been designated as a priority
pollutant by the US Environmental Protection Agency (EPA) and the National
Pollutant Release Inventory (NPRI) of Canada [3]. International regulatory bodies
have set strict discharge limits for phenols for a sustainable environment. For
example, the EPA has set a water purity standard of less than 1 ppb for phenol in
surface water [7]. The toxicity levels usually are in the range of 9–25 mg/L for both
humans and aquatic life [3, 8]. Phenolic compounds are categorized as very harmful
contaminants due to their toxic effects and cancer diseases causing. Short-term
exposure to these compounds results in irritation in human organs, headache,
and inability to balance even at low content, while Long-term exposure to these com-
pounds causing arise in the pressure of blood and very strong kidney and liver
problems [9, 10].

Phenolic compounds removal from water is necessary to protect humans and
aquatics from the pollution that those toxic compounds causing. Appearing a lot of
methods used in the phenolic compounds removing will overcome the hazard
problems connected to these chemicals and wastes discharge challenges, in addition
to, the getting of additional value phenolic compounds as secondary products. A lot
of technologies are used to remove phenolic compounds from wastewater success-
fully before it’s disposal in water resources [3, 7].

Electrochemical oxidation [2, 3, 8], (electro)chemical coagulation [10], solvent
extraction [3], bioremediation [10], and photocatalytic degradation [3, 8], Reverse
osmosis and nanofiltration [2, 8], Chemical oxidation [2, 8], have been used for the
treatment of wastewater from phenolic compounds for many years, but these
techniques are very costly due to the requirements they needed in purification
process as supplementary chemical materials and high input of energy, in addition
to the undesired by-products produced through the treatment process. Therefore,
the separation of phenolic compounds from wastewater requires the development
and using energy-efficient and cheap methods [5, 8, 11–14]. In this Chapter, the
adsorption method is very effective for that purpose. Adsorption is the most effec-
tive method for removing the organic and inorganic contaminants from wastewater
because it is a very easy method to set up, low cost, no time consuming, the
adsorbent used in the process not harmful to the environment and can be recovery
and reused again without the decrease in the efficiency [10]. In the adsorption
method, the removal of pollutants from water occurs by holding them on the
adsorbent surface [2, 11–13]. Carbon-based nanomaterials such as fullerenes, car-on nanotubes (CNTs), graphene and its derivative compounds, nanodiamonds,
and nanoporous carbons (NPC) such as activated carbon are the most popular nano
adsorbent materials used for purification of water between scientists due to their
harmless natural to the environment, abundance, simplicity of handling, and size
and form that give them different properties [15–19]. In this chapter, nanoporous
carbons (NPC) is considered one of the most effective and economical adsorbents used in the separation of organic and inorganic contaminants from the aquatic environment due to their various properties such as high surface area and high porosity, in addition to they are inexpensive, abundance, generate from renewable sources, very thermally stable, and their perfect chemical resistance [20–22]. Furthermore, NPC can attract attention to used in many purposes due to its rule in decreasing the amount wastes in the environment through using them in their preparation process. Their unique properties offer new opportunities in the area of inclusion chemistry, guest host interaction, and molecular manipulations, showcasing their potential impact in a wide range of research fields, such as adsorption, separation, catalysis, electronic devices, and drug delivery [18, 19, 21].

Activation process(such as physical or thermal activation and chemical activation methods) is one of the methods used to prepare nanoporous carbon but due to the disadvantages of this process, the vision has been directed to using the templating method in the preparation process [19, 23].

1.1 The aim of this chapter

To prepare nanoporous carbon materials (NPC) to use in phenolic compound removal, discussing preparation methods, properties of these materials especially activated carbon, and improving these properties to improve the performance of these materials in adsorption application by using templating methods.

2. Phenolic compounds

Nowadays there is a growing concern around the world constantly about the increasing volume of pollutants in the water and the removal of dangerous pollutants from wastewater is one of the most important environmental issues at present. Phenolic derivatives are among the common environmental pollutants. The extremely low concentration of these pollutants is an obstacle to water use. Phenols are toxic and carcinogenic that can cause a bad taste and smell in drinking water also harmful to human health [5, 24]. Phenolic compounds come to water from different various sources such as oil refineries, coal gasification sites, petrochemical units, and from the synthesis of plastics, paints, pesticides, insecticides, pharmaceutical, etc. according to European Union countries, the maximum concentration of phenols in the drinking water is limited to .5 ppb and in the USA to 1 ppb. Both the US Environmental Protection Agency (EPA) and the European Union (EU) involve indicated that nitrophenols and chlorophenols rank first on the pollutant list. The most widespread of phenolic compounds in water is chlorophenol that generates from the chlorination of aromatic compounds that present in water and soil. Phenols have weak acidic properties. (Table 1) discuss the basic information about most phenolic compounds [5, 6, 9].

Diverse technologies have been employed for the removal of phenolic compounds from a variety of water sources including steam distillation, aerobic and anaerobic biodegradation, oxidation by ozone, ion-exchange resins, adsorption, and membrane filtration [11]. But above-mentioned methods, adsorption is the most applied technique for water treatment due to its very simple technique as it works by adding the adsorbent to the polluted water and then target pollutants are adsorbed into the adsorbent, cost-effective, friendly environment and the availability of a wide range of adsorbents. The adsorption of phenol and its derivatives on nanoporous carbon especially activated carbon has become an important issue by many researches [9, 25]. Adsorption is the most applied technique for the removal
| Phenolic compound | pKa at 25 °C | Critical Oxidation Potential (COP) | Boiling point (°C) | Solubility at 25 °C (g l⁻¹) |
|-------------------|-------------|---------------------------------|-------------------|-----------------------------|
| ![Phenolic compound](image1.png) | 9.89 | 1.089 | 182 | 93 |
| ![Phenolic compound](image2.png) | 10.20 | 1.040 | 191 | 25 |
| ![Phenolic compound](image3.png) | 10.01 | 1.080 | 202 | 26 |
| ![Phenolic compound](image4.png) | 10.17 | 1.038 | 202 | 23 |
| ![Phenolic compound](image5.png) | 10.58 | 0.895 | 211 | Unavailable |
| ![Phenolic compound](image6.png) | 10.2 | Unavailable | 207 | Poorly soluble |
| ![Phenolic compound](image7.png) | 10.07 | Unavailable | 214 | Mildly soluble |
| ![Phenolic compound](image8.png) | 10.0 | Unavailable | 218 | Mildly soluble |
| ![Phenolic compound](image9.png) | 8.52 | 1.094 | 204 | 28 |
| ![Phenolic compound](image10.png) | 8.97 | Unavailable | 214 | 26 |
| ![Phenolic compound](image11.png) | 9.37 | 1.094 | 220 | 27 |

Nanopores
of phenolic compounds as it is low cost with high efficiency and easy ergonomic design besides that activated carbon is the most applied adsorbent as it has an internal porous structure (consisting of pores of varying size) with large surface area and specific chemical structure of the surface. And the efficiency of adsorption capacity of phenolic compounds on the activated carbon accompanied by numbers of factors such as:

- Nature of surface functionality of adsorbent and its pore structure
- Properties of adsorbate (phenol) such as pKa, functional group, size, and polarity
- Adsorption parameters such as PH of the solution, temperature, dose of adsorbent, and concentration of adsorbate [24, 25].

There are also important factors such as the type of precursors for Activated carbon preparation and the aqueous solubility of phenolic compounds [9, 11, 26]. Despite extensive studies on factors affecting phenol adsorption, the mechanism of its adsorption is unclear and should be further studied. In particular, the most controversial matter is the role of the presence of oxygen group on its surface in the uptake of phenols [24].

In this study, we have tried to explain the importance of the above factors and how to prepare suitable AC from cheap and available precursors to remove phenolic compounds.

### 3. Historic perspective of nanoporous carbons

Carbon is the most spreading element on the earth, it has distinct characteristics and can form many compounds with different properties. Carbon has been used for a long period in form of coal, charcoal, and carbon black. After that has been discovered a new process to improve the properties of carbon materials through

| Phenolic compound | pKa at 25 °C | Critical Oxidation Potential (COP) | Boiling point (°C) | Solubility at 25 °C (g l⁻¹) |
|-------------------|-------------|---------------------------------|-------------------|--------------------------|
| Phenol            | 7.90        | Unavailable                      | 210               | 4.5                      |
| Chlorophenol      | 5.99        | 1.103                            | 246               | 28.6                     |

Table 1. The basic information about most phenolic compounds [24].
activation of charcoal. These new materials are called nanoporous carbon materials [13, 27, 28].

Carbon was used in past in form of charcoal or carbon black for many purposes:

• It was used as a pigment in the painting of caves from 35000 to 11000 BC.

• Using the carbon in form of charcoal in the production of metal, in 8000 BC.

• Used to decrease minerals in process of bronze fabrication by ancient Egyptians, in 3750 BC

• In medicinal use, since, The first proof was in 1550 BC, where ancient Egyptians used charcoal in the treatment of the stomach tract and removing odors from putrefying injuring.

• In water treatment, since in 450 BC, charcoal filters were used in the treatment of drinkable water [28, 29].

• In the eighteenth century, carbons made from blood, wood, and animals were used for the purification of liquids.

• In the treatment of gases was this observed by the Swedish chemist Karl Wilhelm Scheele in 1773.

• Decolorizing of solutions, experiments on this was performed by Lowitz in 1786.

However, a few years later, in 1794, an English sugar refinery successfully used wood charcoal for decolorization. This application remained a secret until 1812 when the first patent appeared in England, although from 1805 wood charcoal was used in a large-scale sugar refining facility in France for decolorizing syrups, and by 1808 all sugar refineries in Europe were using charcoal as a decolorizer [25, 30].

In 1811, it was proved that the efficiency of decolorization of sugar syrups by bone char was higher than wood char. In 1815, the majority of sugar refining facilities were using granular bone-derived char.

In 1817 Joseph de Cavaillon patented a method of regenerating used bone chars, but the method was not entirely successful [13, 23].

The first example of producing an activated carbon by a combination of thermal and chemical processes was constituted by Bussy In 1822 who demonstrated that the decolorizing abilities of carbons depended on:

• the source material,

• the thermal processing,

• and the particle size of the finished product.

At the beginning of the twentieth century, Raphael von Ostrejko who patented between 1900 and 1903 made a revolution by exploring two distinct methods for the production of nanoporous carbon materials (activated carbon materials) from the activation of charcoal. This scientific breakthrough caused an improving the performance of these carbon materials in many applications by formation a high porosity in carbon materials skeleton.
Because of these discoveries, the first factory for the production of activated carbon materials has been built in Ratibor and was became the oldest factory for activated carbon production in the world [28, 30].

The first application of activated carbon was in World War I, when it was used in manufacturing soldiers masks for protection against hazardous gases and vapors [25].

The production and search for new activated carbons have been boosted decade after a decade due to their fundamental role in various technological applications which are related to, namely, restricted environmental regulations, recovery of valuable chemical compounds, and catalyst support. Nowadays, the driving forces for the research in nanoporous carbons are related to the properties of the most recent carbon materials: fullerenes, carbon nanotubes, and graphene. However, the excellent properties of these novel carbon forms also fostered the interest in the traditional porous carbons and, in 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 [26, 28, 31, 32].

4. Properties of nanoporous carbons

Carbon is one of the most abundant elements on the Earth and plays a critical role in the bio- and ecosystems. Carbon has the unique capability of forming a variety of interesting materials exhibiting extraordinarily different physical and chemical properties [20, 22, 27]. Fullerene [33], carbon nanotubes [33], graphite [15, 34], and diamond [35] are examples. To improve performance, nanoporous structures have been introduced into carbon because nanopores can give a large surface area.

Porous materials have various properties than bulk materials have [27].

- pores are classified according to shapes: cylindrical, spherical, and slit types [4, 29].
- pores are classified according to their accessibility to surroundings into (Figure 1):

![Figure 1. Types of pores according to their accessibility to surroundings [29].](image-url)
Nanopores

- open pores (b,c,d,e,f): pores that interact with the outer surface of the material and they are divided into pores open at one end (b,f) and pores that are open at two ends (e), and these type of pores are used in adsorption, catalysis and sensing processes [29].

- closed pores(a): pores which have no connection to the outer surface (isolated from the surroundings), they result from breakdown the parts close to the external shell of pores due to insufficient heating of porous materials, and these type of pores are used in Lightweight structural applications or thermal insulation [29, 36, 37].

IUPAC (International Union of Pure and Applied Chemistry) proposed the classification of pores according to their size:

- Micropores: pores that have a diameter < 2 nm, they are divided into pores their width less than 0.7 called ultramicropores or narrow micropores and pores in a range of 0.7 and 2 nm called supermicropores or micropores [4, 28].

- mesopores: pores that have a diameter between 2 to 50 nm.

- macropores: pores which have diameter > 50 nm [4, 19, 29, 36–38].

Nanoporous materials are materials with pore size in the range of 1-100 nm [15, 21, 29].

Nanoporous materials have unique features such as high specific surface area, shape-selective effects, fluid permeability, large porosity, and ordered uniform pore configuration. Therefore these materials can be used for many purposes such as separation, sensing, and catalysis applications [19, 39].

| Surface area/porosity | Polymeric | Carbon | Glass | Alumino-silicate | Oxides | Metal |
|-----------------------|-----------|--------|-------|-----------------|--------|-------|
| Low/larger than 0.6   | High/in range 0.3-0.6 | Low/in range 0.3-0.6 | High/in range 0.3-0.7 | Medium/in range 0.3-0.6 | Low/in range 0.1-0.7 |
| Pore size             | Meso-Macro | Micro-meso | Meso-macro | Micro-meso | Micro-meso | Meso-macro |
| Strength              | Medium    | Low    | Strong | Weak            | Weak-medium | Strong |
| Permeability          | low-medium | low-medium | High   | Weak            | low-medium | High   |
| Thermal stability     | Low       | High   | Good   | Medium-high     | Medium-High | High   |
| Chemical stability    | low-medium | High   | High   | High            | Very High   | High   |
| Costs                 | Low       | High   | High   | Low-medium      | Medium     | medium |
| Life                  | Short     | Long   | Long   | Medium-long     | Long       | Long   |

Table 2. Properties of nanoporous materials [39].
Various nanoporous materials with different properties such as surface area, porosity, pore size, thermal stability, etc. [9] are discussed in (Table 2).

The classification of pores discussed above is limited by the data of nitrogen adsorption–desorption at 77 k and that depends on: each pore size has a different mechanism of pore filling determined by isotherm profile [28].

1. Micropore filling: is represented as a primary physisorption divided into two categories:

   - ultramicropores (narrow micropores) filling occurs at low relative pressures (P/P₀ < 0.01) and is controlled completely by the enhanced fluid–solid Adsorption interactions (enhancement of the adsorbent–adsorbate interaction). This process is called (primary micropore filling).

   - supermicropores (wider micropores) filling occurs at a higher relative pressure (P/P₀ in range of 0.01–0.15) and is controlled by cooperative fluid–solid interactions and fluid–fluid interactions.

2. Mesopores filling: occurs through the pore condensation (all adsorbate molecules are in contact with the surface of the adsorbent) followed by the occurrence of multilayer adsorption occurrence and end with capillary condensation due to the sorption process in mesopores relay on fluid–solid interaction and attractive fluid–fluid interactions.

3. The macropores are very large science act as open space, therefore, do not allow the capillary condensation [28, 40].

4. In nanoporous carbons, the porosity results from the spaces between crystallites graphite randomly cross-linked that form the carbon skeleton structure, less ordered carbon materials consumption, and from reactive carbon atoms removal in the crystallite during activation process [28].

4.1 Surface chemistry of nanoporous carbons

The main component of the nanoporous carbon skeleton is carbon atoms, but the basic structure of these materials also contains hydrogen and oxygen and may also include groups containing nitrogen, sulfur, or phosphorus, depending on the precursor, preparation route, and post-synthesis functionalization. Owing to the presence of unsaturated carbon atoms that are extremely reactive, these hetero-atoms are primarily found at the edges of the basal planes. Due to particular interactions with the adsorptive and also the solvent in the case of solution adsorption, the elemental composition, and type of surface groups of a nanoporous carbon affect its efficiency in both gaseous and liquid phase processes. Properties such as hydrophobicity/hydrophilicity or acid/base action are extremely dependent on the surface chemistry of these materials [28, 37, 41, 42].

According to acid/base character, due to the presence of both acid and basic sites on their surface, nanoporous carbons are considered amphoteric materials. Thus, the materials may present net acid, basic or neutral surfaces depending on the amount and the power of all the surface groups [19, 38, 42].

Many methods can be used to evaluate nanoporous carbons surface chemistry and the best way to achieve a good characterization is using the supplementary techniques and incorporation between of the data analysis such as:
• Boehm titrations and potentiometric titrations give qualitative and quantitative data on the nanoporous carbon’s surface.

• diffuse reflectance infrared spectroscopy (DRIFT) and X-ray photoelectron spectroscopy (XPS) give only qualitative information about the surface of the nanoporous carbons.

• and although with less quantitative information temperature-programmed desorption (TPD) detects more oxygen groups than Boehm titration [28, 38, 42].

4.1.1 Acidic surfaces

The chemical nature of nanoporous carbons is determined by surface groups containing oxygen that are mostly located on the external surface or edges of the basal plane.

The amount of oxygen on the surface has a high effect on the nanoporous carbons’ adsorption abilities as these groups constitute the majority of adsorption surface.

These groups can be classified according to chemical nature into three categories: acidic, basic, neutral.

Carboxylic, lactone, phenol, carbonyl, pyrone, chromene, quinone, and ether groups are examples of oxygen-containing functional groups on the nanoporous carbons surface see (Figure 2).

The responsible for surface acidity is Functional groups such as:

Carboxylic acid or carboxylic anhydride, lactone, and phenolic hydroxyl.

These Oxygen-containing functionalities are created by oxidation of carbon surface. The most commonly used activation methods to introduce oxygen-containing acidic groups are oxidation by gases and aqueous oxidants.

• Gas-phase treatment: Oxygen, air, carbon dioxide, and steam can be used in the gas phase treatment. In these processes two routes of oxidation are used:

  ○ oxidation at low temperature can be used to form strong acidic groups (carboxylic).

  ○ oxidation at high temperatures can be used to form a large number of weak acid groups (phenolic).

Figure 2.
Acidic and basic surface functional groups on a carbon basal plane [42].
Liquid phase Treatment: Nitric acid or nitric and sulfuric acid mixture are very effective oxidizing agents due to the introduction of a significant number of oxygenated acidic functionalities onto the carbon surface that mainly includes carboxylic, lactone, and phenolic hydroxyl groups.

A greater quantity of oxygen groups in form of carboxylic and phenolic hydroxyl groups are produced in liquid phase oxidation at much lower temperatures compared to the gas phase oxidation [37, 42].

4.1.2 Basic surfaces

Basicity of activated carbon can be associated with:

i. resonating -electrons of carbon aromatic rings that attract protons,

ii. basic surface functionalities (e.g., nitrogen-containing groups) that are capable of binding with protons.

Chromene, ketone, and pyrone are oxygen-containing surface groups that respond to the nanoporous carbons’ basicity (Figure 2).

The basic character of activated carbons, however, arises primarily from electrons of delocalized graphene-layer. It was proved that these electrons could act as Lewis bases.

The contribution of basal planes to carbon fundamentality has been studied by some researchers. Leon y Leon et al. studied the surface basicity of two carbon series and showed that solution protons can be adsorbed from oxygen-free carbon sites. These sites are found on the basal plane of carbon crystallites in -electron-rich areas. Fundamental sites are therefore the Lewis type associated with the carbon structure itself [42].

Nitrogen-containing functionalities can be introduced through:

- either reaction with nitrogen-containing reagents (such as NH₃, nitric acid, and amines).

- or activation with nitrogen-containing precursors.

Figure 3.
Types of nitrogen surface functional groups: (a) pyrrole, (b) primary amine, (c) secondary amine, (d) pyridine, (e) imine, (f) tertiary amine, (g) nitro, (h) nitroso, (i) amide, (j) pyridone, (k) pyridine-N-oxide, (l) quaternary nitrogen [42].
Possible structures of the nitrogen functionalities include the following: amide group, imide group, lactame group, pyrrolic group, and pyridinic group; which are shown in (Figure 3). Nitrogen functionalities generally provide basic property, which can enhance the interaction between carbon surface and acid molecules such as, dipole–dipole, H-bonding, covalent bonding, and so on [37, 41, 42].

4.2 Nanoporous carbons analysis

Nanoporous carbons are used in various applications such as separation, catalysis and energy storage, and so on [19]. The properties of these materials depend on the application used. Therefore, characterization of these materials is very necessary to determine the properties of materials before use in experimental applications. Surface area, pore size, and porosity are important properties in the fields of catalysis, separation, batteries, gas and energy storage, and others.

As selectivity, diffusional rates and transport phenomena are important properties in catalyzed reactions, determining the pore structure in-depth is very necessary as it controls these properties.

Various techniques can be used for this purpose such as:

- gas adsorption analysis (physical adsorption)
- small-angle X-ray (SAXS)
- small-angle neutron scattering (SANS)
- Mercury intrusion porosimetry
- Nuclear magnetic resonance (NMR-based methods)
- scanning electron microscopy
- transmission electron microscopy
- thermoporometry,
- Brunauer, Emmett, and Teller (BET) technique

Each approach has a small applicability length scale for the study of pore size. The International Union of Pure and Applied Chemistry (IUPAC) gave a detailed overview of the various methods for characterizing pore size and their application range [43–45].

Gas adsorption is a common one among these, as it allows a wide variety of pore sizes to be examined, including the full range of micro-and mesopores. Moreover, as opposed to some of the methods described above, gas adsorption techniques are easy to use, are not harmful, and are not expensive [45].

4.2.1 Adsorption process

In general, adsorption is defined as the enrichment of molecules, atoms, or ions in the vicinity of an interface. In the case of gas/solid systems, adsorption takes place in the vicinity of the solid surface and outside the solid structure. The material in the adsorbed state is known as the (adsorbate), while the adsorptive is the same component in the fluid phase. The adsorption space is the space occupied by the adsorbate. Adsorption can be physical (physisorption) or chemical (chemisorption) [1, 5, 46].
4.2.1.1 Chemical adsorption: (chemisorption)

In chemisorption, the intermolecular forces involved lead to the formation of chemical bonds. When the molecules of the adsorptive penetrate the surface layer and enter the structure of the bulk solid, the term absorption is used. It is sometimes difficult or impossible to distinguish between adsorption and absorption: it is then convenient to use the wider term sorption which embraces both phenomena, and to use the derived terms sorbent, sorbate, and sorptive [1, 46].

4.2.1.2 Physisorption: (physical adsorption)

Is widely used for the surface and textural characterization of nanoporous materials (e.g. for textbooks and reviews see: Sanghi, Canevesi, Celzard, Thommes [40], and Fierro. 2020 [4]; Thommes 2015 [46]; Thommes 2014 [40]) [40]. Physisorption is a general phenomenon and occurs whenever an adsorbable gas (the adsorptive) is brought into contact with the surface of a solid (the adsorbent). The forces involved are the van der Waals forces. Physisorption in porous materials is governed by the interplay between the strength of fluid–wall and fluid–fluid interactions as well as the effects of confined pore space on the state and thermodynamic stability of fluids in narrow pores [6, 7, 40].

There has been considerable progress over the last two decades in understanding sorption phenomena in small pores, which in turn has contributed to substantial progress in physical adsorption.

The development and application of microscopic methods, such as functional density theory (DFT) of inhomogeneous fluids (e.g., nonlocal density functional theory, NLDFT) or computer simulation methods such as Monte Carlo (MC) and molecular dynamic (MD) simulations, is closely correlated with this advancement [29]. Among many porous materials, nanoporous carbons (NPC), with interpenetrated and regular nanopore systems, have recently triggered enormous research activities because of their fascinating chemical and physical properties, such as high specific surface area, tunable pore structure, catalytic activity, high thermal and chemical stability, intrinsic high electrical conductivity, low density, and wide availability. Therefore, they have been implemented in hydrogen storage, pollutant adsorption, energy storage, (i.e., batteries, supercapacitor), catalysts, energy conversion, and electrochemical devices [19, 27, 36, 37].

5. Nanoporous carbon materials synthesis

Various natural biomass such as cassava peel waste, chicken eggshell, seed shell, rubberwood sawdust, wood, peanut kernel, lignocellulose (biomass) materials, corn cob, Kraft lignin, scrap tires, textile waste, rice husk, palm shell, and sugar have been employed as precursors for the production of NPC. These sources are generally rich in carbon giving amorphous phases, and the plant wastes containing the cellulose are familiar to form graphitic nanostructures with high-temperature treatments [47].

Conventional porous carbon materials, such as activated carbon, have routinely been prepared by pyrolysis followed by the activation process of the organic precursors, such as coal, plant, wood, or polymers, at specific high temperatures [19].

5.1 Activation

Carbonaceous materials are activated to create porosity, controlled morphology, and functional groups on the surface. The pyrolysis process is generally carried out
before undergoing the activation process as the former process generates organic residues, which may block the porous channels of the final carbon materials. Physical and chemical activation are two preferred choices for the fabrication of nanoporous carbon materials from carbon-rich precursors, including waste materials [47, 48] (Table 3).

5.2 Physical or thermal activation

Physical activation is usually carried out in two consecutive heating stages: Carbonization of the raw material under the inert atmosphere (usually nitrogen) to devolatilize the raw material, accompanied by activation consisting of partial gasification of the char acquired with oxidizing agents (i.e., steam, carbon dioxide or a combination of both) leading to the creation of a porous network.

While carbonization normally occurs at temperatures between 400 and 600 °C, temperatures ranging from 800 to 1000 °C are needed for gasification.

It is also possible to skip the carbonization stage, depending on the raw material, and proceed directly to thermal activation [47, 48].

- CO₂ is considered the preferred choice for physical activation due to the ease of handling, control of various parameters, and slow reaction rate. Instead of

| Type of activation | Activating agent | Suitable precursors | Type of Porosity | The general trend of experimental conditions on pore size distribution (PSD) |
|--------------------|------------------|---------------------|------------------|--------------------------------------------------------------------------------|
| Physical           | CO₂              | Coals and, to less extend, hard lignocellulosic materials | Micro only       | • The high degree of activation contributes to a high size of micropores with a similar pore sizes distribution |
| Steam              |                  | Coals and, to less extend, hard lignocellulosic materials | Micro and meso   | • High activation degree leads to Widening of pore sizes distribution and obtaining on Micro and mesopore networks |
| Chemical           | ZnCl₂            | High volatile and oxygen content materials (Lignocellulosic materials) | Micro and meso   | • Uniform micropore size distribution which broadening with the increase of the Zn/precursor ratio to the micro/mesopore boundary |
|                    | H₃PO₄            | High volatile and oxygen content materials (Lignocellulosic materials) | Micro and meso   | • Pore Size Distribution primarily in the border of micro/mesopore boundary and based on the temperature of heat treatment (<450 °C). |
|                    | KOH              | Low volatile and high carbon content materials (coals of the High rank) | Micro only       | • The KOH/precursor ratio has a greater effect on the capacity of adsorption and PSD than the activation temperature. • Increasing the KOH/precursor ratio widens pores from narrow to large micropores and to small mesopores in a lesser extent; also hinders the morphology of granules (particle disintegration leads to powders). |

Table 3. Appropriate precursors, kinetic of activation, and type of porosity are typically obtained for the most common activating agents [28].
diffusional regulation which is quicker but contributes to external particle burning and, ultimately, to poor production of porosity. CO₂ activation must occur in conditions that ensure chemical control (slow activation rate-days).

The reactions of steam and carbon dioxide with carbon are endothermic, thus:

To sustain the necessary high temperature, thermal activation requires an external energy supply [28, 31].

- Oxygen (or air) is not widely used as an oxidizing agent because its carbon reaction is highly exothermic and rapid, and instead of particle consumption, it is difficult to monitor and ensure porosity growth. Oxygen activation is scarcely used because of this and the safety concerns associated with temperature regulation.

However, low amounts of oxygen (or air) may be added to steam or carbon dioxide during thermal activation to help sustain high temperatures by responding to the gases emitted during activation (i.e. CO and H₂).

This strategy has the benefit of decreasing CO and H₂ pressure, both inhibiting activation gases and increasing the triggering agent’s partial pressure [28] (Table 3).

5.3 Chemical activation

Chemical activation normally needs just one heating step: the raw material is combined with an activating agent (e.g. ZnCl₂, H₃PO₄, KOH) and further treated at temperatures between 400 and 900 °C under a controlled atmosphere, depending on the activating agent selected. The activating agent helps to remove the residual water moieties from the raw materials by acting as a dehydrating agent and also assists as an oxidant. Both the processes affect the decomposition of precursors and rearrangement of the resulting carbon atoms into an aromatic framework (Table 3).

Chemical activation offers an additional advantage of introducing functional groups such as -COOH, -NH, or -OH on the surface of the porous carbon. However, the crystallinity of the sample after the chemical activation is reduced due to the continuous dehydration and the oxidation with the activating agent, which creates a lot of defect sites along the carbon walls of the final product [28, 47, 48].

The mechanism of pore formation depends, in this process, on the chemical agent:

- Zinc chloride facilitates the elimination of water molecules from the raw material’s lignocellulosic structures.
- Chemically, phosphoric acid merges with them.
- The selective removal of carbon atoms happens in none of these systems.
- The method is more complicated with potassium hydroxide as the structure is disintegrated and the metallic potassium is intercalated into the “graphic” laminar structure, particles are broken down and granular activated carbon synthesis is prohibited. At the same time, due to reaction with CO₂ and H₂ O, resulting from the redox reaction of carbon with potassium compounds, there is also some gasification of carbon atoms. The lignocellulosic precursor loses volume by contraction during carbonization (i.e. heat treatment under inert
atmosphere), but when chemical activation is applied, the activating reagent is incorporated into the particles which inhibit the anticipated contraction, i.e. the activating agent will act as a template for microporosity formation. [28, 31, 32, 48, 49].

Chemical activation has advantages over the physical process discussed in (Table 4).

5.4 Other nanoporous carbons synthesis methods

The chemical activation process using KOH, K2CO3, K2O, ZnCl2, KHCO3, H3PO4, etc., and their reaction are very useful to make nanopores, however, harsh reaction condition, cost of required chemicals and processes, residue, ununiformed pore distribution, and difficult control of pore size should be considered for upscaling the production and commercialization. Compared with chemical activation, physical activations utilizing mainly CO2 and steam activation usually has a high yield and bulk density but suffers from a relatively low surface area and pore volume due to the lower degree of carbon etching. Therefore, many researchers have studied the efficiency of other methods to fabricate nanoporous carbon materials. Thus, hard- and soft-templating approaches have been successfully introduced for the preparation of NPC with well-defined pore structures and narrow pore size distributions. In this Chapter, the hard- and soft-templating synthesis are introduced as potential approaches for the preparation of NPC materials with a special emphasis on the progress and developments in the methodology.

Hard synthesis of templates requires the use of pre-synthesized organic or inorganic templates, while the soft synthesis of templates depends on the creation of nanostructures through self-assembling organic molecules [19, 23].

5.4.1 Templating method

Historically, Knox and co-workers, who demonstrated the synthesis of graphitic porous carbons for liquid chromatography separation by impregnation of spherical

| Chemical activation | Physical activation |
|---------------------|---------------------|
| Advantages           |                     |
| • One step          | • Utilizing mainly CO2 and steam activation |
| • Energy saving     | • Has a high yield  |
| • Higher yields     | • Has a high bulk density |
| • Shorter activation time (hours) |                     |
| • High surface area |                     |
| • High pore size.   |                     |
| Disadvantages       |                     |
| • Harsh reaction condition | • Relative low surface area and pore volume due to the lower degree of carbon etching. |
| • Low recovery efficiencies | • Two consecutive heating steps |
| • Time-consuming (washing to remove chemical residue. |                     |
| • Cost of required chemicals and processes Residue. |                     |
| • Some activating agents are harmful (ZnCl2 and H3PO4). |                     |
| • Ununiformed pore distribution. |                     |
| • Difficult control of pore size. |                     |

Table 4. Advantages and dis advantages of activation processes [28, 48].
porous silica gel particles with phenolic resin and subsequent carbonization and silica removal, first reported the templating process in 1986. This technique has gained considerable attention since then and different types of template carbons are synthesized. The resulting carbon synthesized by the templating method has a relatively narrow PSD and regulated architecture called a templated carbon.

The templated carbonization method permits one to control the carbon structure in terms of various aspects, such as pore structure, specific surface area, microscopic morphology, and graphitizability, which makes this method very attractive [48].

Porous materials are fabricated in several different ways. The Hard Template Method and Soft Template Method are the two most common methods to make porous materials [39, 50, 51].

5.4.1.1 Hard template method

The most common hard template synthetic route for mesoporous carbon materials was first reported by Knox et al. using a spherical solid gel as the template. Highly ordered NPC with oriented mesoporous structures can be obtained using the hard template method.

The hard template method includes the following steps: (a) synthesis of a suitable porous template; (b) introduction of a suitable carbon precursor into the template pores using the method of wet impregnation, chemical vapor deposition, or a combination of both methods; (c) polymerization and carbonization of the carbon precursor; and (d) removal of the inorganic template. Following these steps, porous carbon with a specific pore structure is formed [19, 48, 52].

Angelina Sterczyńska, Małgorzata Śliwińska-Bartkowiak, Małgorzata Zienkiewicz-Strzałka, Anna Deryło-Marczewska Synthesized Nanoporous Carbon (also called ordered mesoporous carbon material [OMC]) with a 4.6 nm pore size, and ordered silica porous matrix, SBA-15, with a 5.3 nm pore size [54].

Also, Dandan Guo, Jin Qian, Ranran Xin, Zhen Zhang, Wei Jiang, Gengshen Hu, Maohong Fan prepared Mesoporous carbons enriched with nitrogen by hard template method for supercapacitors. Where CCl₄ and ethylenediamine (EDA)
represent precursors whereas silica act as a hard template [53] (see Figure 4). While Wei Liu, Hong Yuan, and Yihu Ke Prepared ordered mesoporous carbon-based on soybean oil by using the hard template method where a hard template is represented by ordered mesoporous SiO$_2$ molecular sieves (SBA-15) [55].

However, when extracting from the template, the sacrificing of the solid template and mesoporous NPC structures limits the usefulness of hard template synthesis. The use of soft template synthesis will overcome these constraints [51, 54, 56].

5.4.1.2 The soft template method

The soft template is a kind of surfactant, which has a strong interaction with the carbon source, and mesoporous carbons with different structures can be obtained through the soft template method. This method possesses good controllability and operability; as a result, it has very good application prospects. The mechanisms of the soft template method include a liquid-crystal template mechanism, a synergistic assembly mechanism, a “rod micellar” mechanism, and so on; these mechanisms have been widely recognized [48, 52].

Amphiphilic molecules, such as surfactants and block copolymers, have been extensively used as soft-templates in the synthesis of ordered mesoporous materials. The discovery of ordered mesoporous carbon materials appeared to have a great impact in this field because of the fascinating features of their unique physical and chemical properties which can surmount the shortcomings in various technological applications. Preparing these ordered mesoporous carbons can be difficult to achieve by a simple self-assembly method for many reasons, although recent reports have demonstrated that polymeric micelles can serve as templates for mesoporous carbons. The key requirements for a successful synthesis using the soft-templating method are (i) the ability of the precursor species, such as the copolymers and the carbon source, to self-assemble into nanostructured polymer composite, (ii) the presence of at least one performing species, and one carbon source, (iii) the stability of the pore-forming species which can endure the temperature required for thermally decomposing the

Figure 5.
Soft-templating synthesis of carbon nitride and graphene materials. Route 1: (1-a) self-assembly of surfactant or block copolymer molecules (1) into micelles (1-1-a), (1-b) addition of a carbon nitride precursor and formation of micelle-precursor mesostructures (1-1-b), (1-c) initial condensation/polymerization of the precursor, (1-d) further condensation and template elimination creating a nanoporous carbon nitride material (1-1-d), (1-e*) initial condensation of the precursor conducted at a temperature higher than the decomposition point of the soft template, (1-d*) further condensation but causing structural collapse. Route 2: (2-a) addition of a carbon precursor and production of individual micelle-carbon precursor units, (2-b) close-packing of these units on a substrate (side view, depicted in gray) forming a monolayer (1-2-b), (2-c) polymerization of the carbon precursor followed by carbonization, (2-d) graphitization giving nanoporous graphene sheets. Black lines represent the 2D building units, namely carbon nitride or graphene layers [19].
carbon source during carbonization process, and finally (iv) the ability of the carbon source to form cross-linked polymers that can retain their nanostructures during the thermal decomposition. The synthesis principles of these self-assembled nanostructured mesoporous carbons open the way for the development of new strategies for materials in the future. Researchers have reported that only a few materials meet the requirements for the successful synthesis of ordered mesoporous carbons using a soft-templating approach [23, 50, 56]. Some of the research activities related to the soft-templating synthesis of polymeric structures are summarized [19] (see Figure 5).

6. Activated carbon as the essential phenol removal adsorbent

6.1 The activated carbon precursors

There is a wide range of raw materials that can be successfully used as a precursor for the preparation of activated carbon. Almost interesting precursors have been obtained from any carbonaceous materials such as agricultural waste, wood, petroleum coke, and industrial biomass. An important aspect in the preparation of activated carbon is the use of different parts of plants including the pulp, stems, shells, peels, flowers, fruits, seeds, stones, peels, and leaves. All these precursors can be carbonized and then activated under desired conditions to yield activated carbon [25]. The selection of the precursors is based mainly upon the following several factors:

- High carbon content and low amount of ash.
- Availability and inexpensive.
- Low content of inorganic matter.
- Nonhazardous for nature.

| Raw Material | Carbon (mass%) | Volatiles (mass%) | Density (cm$^3$ g$^{-1}$) | Ash (mass%) | The texture of activated carbon |
|--------------|----------------|------------------|--------------------------|------------|-------------------------------|
| Soft wood    | 40–45          | 55–60            | 0.4–0.5                  | 0.3–1.1    | Soft, large pore volume       |
| Hard wood    | 40–42          | 55–60            | 0.55–0.8                 | 0.3–1.2    | Soft, large pore volume       |
| Lignin       | 35–40          | 58–60            | 0.3–0.4                  | —          | Soft, large pore volume       |
| Nutshells    | 40–45          | 55–60            | 1.40                     | —          | Hard, large micropore volume  |
| Lignite      | 55–70          | 25–40            | 1.0–1.35                 | 5–6        | Hard, small pore volume       |
| Soft coal    | 65–80          | 20–30            | 1.25–1.5                 | 2–12       | Medium hard, medium pore volume |
| Petroleum coke | 70–85        | 15–20            | 1.35                     | 0.5–0.7    | Medium hard, medium pore volume |
| Semi-hard coal | 70–75        | 10–15            | 1.45                     | 5–15       | Hard, large pore volume       |
| Hard coal    | 85–95          | 5–15             | 1.5–1.8                  | 2–15       | Hard, large pore volume       |

Table 5. Properties of some raw materials and the properties of activated carbon generated [24].
The characteristic of activated carbons such as physicochemical properties that responsible for carbon adsorption properties and other possible applications depend on selected carbon precursors in addition to the preparation method. Lately, it is longer than lignocellulosic resources and waste biomass is the most used precursors for the production of the activated carbon (Table 5). Summary of the properties of some raw materials and the properties of activated carbon generated [24, 57, 58].

The usage of lignocellulosic biomass in the generation of activated carbon has many features as it is renewable and most abundant in nature, inexpensive, and helps to dispose of its negative impact effect on the environment. Numerous reviews have been devoted to inexpensive precursors of activated carbon in recent years [58, 59].

6.2 Generation of porosity and surface chemistry (activated carbon)

All activated carbon is generally characterized by a porous structure with their high surface area, usually have few amounts of chemically bounded heteroatom oxygen, hydrogen, sulfur, and nitrogen. Beside may contain around 20% by weight of a mineral substance called ash content [24, 49]. It is known that the surface of activated carbon has a high heterogeneous phenomenon. AC surface heterogeneity comes from two various sources called geometrical and chemical sources. Geometric heterogeneity results from differences in the size and shape of pores, cracks, pits, and steps. Chemical heterogeneity is associated with different functional groups, especially the oxygen groups that are most often found at the edges of turbine crystals, as well as with various surface impurities. The heterogeneity of AC (Geometric, Chemical) surfaces affect unique adsorption properties. The chemical properties and structure of activated carbon and its structure can be changed depending on the type and nature of presence and number of oxygen functional groups on its surface [24, 25, 36, 59].

It’s possible to produce activated carbon from all carbonaceous materials which its preparations involve two major steps: carbonization of the precursors followed by activation method as shown in (Figure 6). Carbonization means the conversions of raw materials at elevated temperatures into a highly stable carbon structure with an elementary and partially-developed pore structure. During this step, water and volatile substances are removed leaving the char behind. Followed by activation of char by physical or chemical activation to produce highly porous activated carbon. The generated activated carbon characterize by having a porous structure, high
surface area, and highly reactive surface functionality. Physical activation involves the carbonization of the precursors in the presence of inert gas in the range between 500 to 900 °C followed by gasification of the resulting char with carbon dioxide. Steam, air, or mixtures of both can be also used as activating agents. Excessive temperatures lead to reduced carbon content, collapse its pore structures and increase ash generation. in physical activation, proper temperature and time are so important to achieve adequate pore development and the creation of functional groups. In chemical activation, the raw material is directly impregnated with an activating agent such as KOH, NaOH, H$_3$PO$_4$, H$_2$SO$_4$, HNO$_3$, ZnCl$_2$, and FeCl$_3$, and the impregnated product is pyrolyzed at high temperature for a certain time and then product washed to remove the activating agent. The activating agent can contribute in the oxidation and gasification the carbon precursors to improve porosity and transform surface functional group. The pores generated from activation are usually identified as micropores and mesoporous [24, 28, 48]. Chemical activation has advantages among physical included in (a)-the low temperature of activation. (b) Well developed in the porous structures.

Different pore sizes (micro, meso, and macropores) are obtained depending on the nature and type of precursors, activating agent, and reaction conditions such as time and temperature. The properties of raw material such as its type and size, the type of activating agent, the ratio of mixing raw material with the activating agent, the conditions of heating in the furnace, will have a significant effect on the characteristics of the final product including surface area and pore size [24, 48]. However, first and foremost, the adsorption features of activated carbon are dictated by its chemical composition. The existence of hydrogen and oxygen groups on the surface of the activated carbon directly affects the adsorption performance. Original AC precursors, the activation process, or post-treatment after the preparation process can be the source of these surface groups. The oxygen groups are mainly formed on the surface of activated carbon following activation by air exposure or by relevant post-treatment [25, 57, 60, 61].

Carbon is more likely to chemisorb oxygen than any other species. Chemisorbed oxygen present on the surface of AC to form carbon and oxygen functional groups can be acidic, neutral, or basic. The formation of oxygen groups on the carbon surface is generated from the reaction with the activating agent used such as (H$_2$SO$_4$, HNO$_3$, H$_2$O$_2$) and other oxidizing gases like CO$_2$ and O$_3$. Among the factors affecting the nature of the surface group of oxygen, the temperature may be taken into account, as surface acidity is formed that includes carboxyl functional groups, carboxylic anhydrides, lactones, and phenol hydroxyls upon exposure to low temperature while basic surface that generated from delocalized $\pi$-electrons on a carbon basal plane like pyrone, quinone, and carbonyl generated at high temperature [24].

To define the number of groups of oxygenated surfaces, The Boehm titration method is used. The basic functional groups are the most preferred than the acidic functional group for the adsorption of phenolic compounds. And some experimental methods like temperature-programmed desorption (TPD), infrared spectroscopy, acid–base titration, X-ray photoelectron spectroscopy (XPS), can be used to characterize surface-oxygen groups [24, 57].

6.3 Role of surface heterogeneity on adsorption of phenol

Although activated carbon has been investigated for a long time as an effective adsorbent of organic pollutants, the exact structure of the functional groups and the mechanism of phenolic compounds adsorption is not well understood yet. Much information should be considered before applied adsorption of phenol such as:
1. The effects of surface functionalities on adsorption phenols exhibit a complex significance than the porosity effect.

2. Activated carbon have an amphoteric character in an aqueous solution (possesses both, acidic and basic surface functional groups) and has a positive or negative charge on its surface depending on the solution of PH. The type of nature of activated carbon surface affects the adsorption of organic electrolytes such as phenol so it is so important to determine the charge of the surface of activated carbon as well as the extent of ionization of the phenol before the application of phenol adsorption [41].

3. The chemical characteristics on activated carbon surface determine from functional groups and π-delocalized electrons of fused aromatic structures. The affinity of the activated carbon toward adsorbate can be determined from the content of surface functional groups and pHpzc. The pHpzc indicates zero net surface charge of the adsorbents that implies their electronic surface charges. The surface is positively charged at pH < pHpzc in which water gives protons more than the hydroxyl group and when pH > pHpzc the surface has a negative charge. It is commonly assumed, that for pH < pK<sub>a</sub> adsorption of non-ionized organics does not depend on the surface charge of AC. However, for pH > pK<sub>a</sub> the phenolic compound is dissociated, and adsorption of its ionic form depends on the surface charge.

4. In the case of phenolic adsorption, the basic surface of activated carbon is so preferred to achieve high performance of adsorption of phenol.

The adsorption capacity of phenol on activated carbon depends on some factors such as:

a. The solubility of phenols in water.

b. The degree of activation.

c. The hydrophobicity of substituted phenols [24, 25, 42].

And thus adsorption capacity increase with increasing specific surface area and porosity while it decreases by the solubility of phenolic compounds in water and increases the hydrophobicity of phenolic substituted. For example, phenolic compounds that having low solubility in water like p-cresol and p-nitrophenol are adsorbed on activated carbon than other phenols. On the other hand, chlorophenol, nitrophenol, cresol adsorbed greater on activated carbon than phenol and aminophenol due to their hydrophobic group. The adsorption of phenolic compounds onto the ACs mainly contribute to three types of interactions namely, (i) π-π dispersion interaction, (ii) the electron-donor–acceptor complex formation, and (iii) the hydrogen-bonding formation. The mechanism of adsorption of phenolic compounds toward activated carbon occurs through the formation of electron donor-acceptor complex between the aromatic ring of phenol and basic sites on the surface of activated carbon (basic surface oxygen complex and/or z-electron-rich sites on the basal planes). Therefore, the relative affinity between the carbon surface’s basic characteristic and aromatic phenolic ring increases. Electron withdrawing of phenolic rings tends to form electron donor-acceptor complex between these ring and basic sites on the surface of activated carbon [24, 25, 42]. In the case of oxidation, the surface of activated carbon with a strong oxidizing agent leads to the
formation of the acidic surface with a large quantity of carboxyl and phenolic groups with a small amount of carbonyl and chromene lead to inhibition of phenol adsorption. During the adsorption of phenol on activated carbon, these regions act as a donor and the aromatic rings of phenol as acceptors. Phenol adsorption onto the activated carbon is controlled by dispersive force between $\pi$ electrons. The interaction of $\pi$-$\pi$ dispersion occurs between basal planes of activated carbon and the phenol aromatic ring [24, 42]. The change in pH solution affects phenol adsorption. The adsorbed amount of PH decrease at low and high pH values. At low pH value, protons were added to compete with the adsorbate for the carbonyl sites leading to a reduction of adsorption of phenol at this value. Besides the surface chemistry of activated carbon, the pore structure also affects the adsorption process. The porosity of activated carbon has been considered an important factor in the adsorption processes of phenolic compounds from aqueous solutions. The adsorption capacity of small molecules such as phenol to the inner surface of carbon correlates with the content of micropores and BET surface area, while for mesoporous ACs, substituent group in the phenol and nature of the carbon controlled the phenol adsorption as well [24, 37, 38, 41].

7. Conclusion

Nanoporous carbon materials have an attractive rate performance in many applications of recent technology such as pollutant adsorption. In this chapter, the properties of nanoporous carbon and its various preparation methods are presented. Also, our choice of the preparation method, reaction conditions, and the precursor materials affect the properties of the resulting nanoporous structure. The adsorption of phenolic compounds from polluted water is one of the most common uses of nanoporous carbon, especially activated carbon in water treatment. Numerous factors are known to have an important influence on phenolic adsorption like the type of carbon structure, functional groups present on the surface, oxygen availability on its surface, pH value of the aqueous media, etc. Furthermore, there are several scientific papers reviewed - aspects most relevant to indicating today’s trends and potential insights in elucidating the adsorption mechanisms of phenolic compounds on activated carbon.

Appendices and nomenclature

Nanoporous carbon materials: (NPC).
Nanopores

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References

[1] Singh, S., et al. (2020). Chapter 10 - Low-cost adsorbents for removal of inorganic impurities from wastewater. Inorganic Pollutants in Water. P. Devi, P. Singh and S. K. Kansal, Elsevier: 173–203.

[2] Eduardo Enrique Pérez Ramírez, Miguel de la Luz Asunción, Veronica Saucedo Rivalcoba, Ana Laura Martínez Hernández and Carlos Velasco Santos (March 15th 2017). Removal of Phenolic Compounds from Water by Adsorption and Photocatalysis, Phenolic Compounds - Natural Sources, Importance and Applications, Marcos Soto-Hernandez, Mariana Palma-Tenango and Maria del Rosario Garcia-Mateos, IntechOpen, DOI: 10.5772/66895. Available from: https://www.intechopen.com/books/phenolic-compounds-natural-sources-importance-and-applications/removal-of-phenolic-compounds-from-water-by-adsorption-and-photocatalysis.

[3] William W. Anku, Messai A. Mamo and Penny P. Govender (March 15th 2017). Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods, Phenolic Compounds - Natural Sources, Importance and Applications, Marcos Soto-Hernandez, Mariana Palma-Tenango and Maria del Rosario Garcia-Mateos, IntechOpen, DOI: 10.5772/66927.

[4] Sdanghi G, Canevesi RLS, Celzard A, Thommes M, Fierro V. Characterization of Carbon Materials for Hydrogen Storage and Compression. C. 2020; 6(3):46. https://doi.org/10.3390/c6030046

[5] Wang, J., et al. (2020). "Degradation of phenolic compounds by dielectric barrier plasma: Process optimization and influence of phenol substituents." Chemical Engineering Journal 385: 123732.

[6] Tri, N. L. M., et al. (2020). “Removal of phenolic compounds from wastewaters by using synthesized Fe-nano zeolite.” Journal of Water Process Engineering 33: 101070.

[7] Asencios, Y. J. O., et al. (2020). “Removal of phenol in seawater by heterogeneous photocatalysis using activated carbon materials modified with TiO2.” Catalysis Today.

[8] Villegas, L. G. C., et al. (2016). “A Short Review of Techniques for Phenol Removal from Wastewater.” Current Pollution Reports 2(3): 157–167.

[9] Nakagawa, K., et al. (2004). “Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes.” Water Research 38(7): 1791–1798.

[10] Turco A, Monteduro AG, Mazzotta E, Maruccio G, Malitesta C. An Innovative Porous Nanocomposite Material for the Removal of Phenolic Compounds from Aqueous Solutions. Nanomaterials. 2018; 8(5):334. https://doi.org/10.3390/nano8050334

[11] Chen, M., et al. (2018). "Methane adsorption behavior on shale matrix at in-situ pressure and temperature conditions: Measurement and modeling." Fuel 228: 39–49.

[12] Duan, J., et al. (2021). “Simultaneous adsorption of uranium (VI) and 2-chlorophenol by activated carbon fiber supported/modified titanate nanotubes (TNTs/ACF): Effectiveness and synergistic effects." Chemical Engineering Journal 406: 126752.

[13] Jiang, L., et al. (2020). “Role of adsorption and oxidation in porous carbon aerogel/persulfate system for non-radical degradation of organic
contaminant." Chemosphere 241: 125066.

[14] Kong, L. and H. Adidharma (2018). “Adsorption of simple square-well fluids in slit nanopores: Modeling based on Generalized van der Waals partition function and Monte Carlo simulation." Chemical Engineering Science 177: 323–332.

[15] Tofighy, M. A., et al. (2020). Chapter 6 - Development of advanced nanocomposite membranes by carbon-based nanomaterials (CNTs and GO). Nanocomposite Membranes for Water and Gas Separation. M. Sadrzadeh and T. Mohammadi, Elsevier: 145–162.

[16] Singh, S., et al. (2020). Chapter 10 - Low-cost adsorbents for removal of inorganic impurities from wastewater. Inorganic Pollutants in Water. P. Devi, P. Singh and S. K. Kansal, Elsevier: 173–203.

[17] Gusain, R., et al. (2019). “Recent advances in carbon nanomaterial-based adsorbents for water purification." Coordination Chemistry Reviews 405.

[18] Gopalakrishnan, K. (2015). Nanocarbons for Advanced Energy Storage, Volume 1, DO - 10.1002/9783527680054.ch8.

[19] Malgras, V., et al. (2019). “Fabrication of Nanoporous Carbon Materials with Hard- and Soft-Templating Approaches: A Review." J Nanosci Nanotechnol 19(7): 3673–3685.

[20] Yu, L., et al. (2020). “Solvent-free synthesis of N-doped nanoporous carbon materials as durable high-performance pH-universal ORR catalysts." Journal of Colloid and Interface Science 575: 406–415.

[21] Van Riet, R., et al. (2020). “Novel opportunities for nanoporous carbons as energetic materials." Carbon 164: 129–132.

[22] Gomis-Berenguer, A., et al. (2016). “Sulfur-mediated photochemical energy harvesting in nanoporous carbons." Carbon 104: 253–259.

[23] Haynes, T., et al. (2020). “Preparation of mesoporous silica nanocapsules with a high specific surface area by hard and soft dual templating approach: Application to biomass valorization catalysis." Microporous and Mesoporous Materials 306: 110400.

[24] Dąbrowski, A., et al. (2005). “Adsorption of phenolic compounds by activated carbon—a critical review." Chemosphere 58(8): 1049–1070.

[25] Water and Wastewater Treatment: Historical Perspective of Activated Carbon Adsorption and its Integration with Biological Processes. Activated Carbon for Water and Wastewater Treatment: 1–11.

[26] Hassan, A. F. and H. Elhadidy (2017). “Production of activated carbons from waste carpets and its application in methylene blue adsorption: Kinetic and thermodynamic studies." Journal of Environmental Chemical Engineering 5(1): 955–963.

[27] Marpaung, Freddy, Synthesis of nanoporous carbon derived from hybrid metal organic frameworks for symmetric supercapacitor, Master of Philosophy thesis, Institute for Superconducting and Electronic Materials, University of Wollongong, 2019. https://ro.uow.edu.au/theses1/780

[28] Ana S. Mestre and Ana P. Carvalho (December 20th 2017). Nanoporous Carbon Synthesis: An Old Story with Exciting New Chapters, Porosity - Process, Technologies and Applications, Taher Hcine Ghrib, IntechOpen, DOI: 10.5772/intechopen.72476. Available from: https://www.intechopen.com/books/porosity-process-technologies-and-applications/nanoporous-carbon-
synthesis-an-old-story-with-exciting-new-chapters

[29] Zdravkov, B. D., et al. (2007). “Pore classification in the characterization of porous materials: A perspective.” Central European Journal of Chemistry 5(4): 1158–1158. The original version of the article was published in Cent. Eur. J. Chem., Vol. 5(2), (2007), pp. 385–395. It can be also found online at: http://dx.doi.org/10.2478/s11532-007-0017-9.

[30] Kerimkulova, A., et al. (2017). “Synthesis and application of carbon adsorbents in chromatographic separation of biologically active complexes.” Frontiers in Nanoscience and Nanotechnology 3.

[31] Luo, H., et al. (2018). “Self-terminated activation for high-yield production of N,P-codoped nanoporous carbon as an efficient metal-free electrocatalyst for Zn-air battery.” Carbon 128: 97–105.

[32] Huang, J., et al. (2020). “In-situ synchronous carbonation and self-activation of biochar/geopolymer composite membrane: Enhanced catalyst for oxidative degradation of tetracycline in water.” Chemical Engineering Journal 397: 125528.

[33] Sirivisoot, S. and T. J. Webster (2011). 5.523 - Carbon Nanotubes: Applications for In Situ Implant Sensors. Comprehensive Biomaterials. P. Ducheyne. Oxford, Elsevier: 303–315.

[34] Mortazavi, B., et al. (2019). “Nanoporous graphene: A 2D semiconductor with anisotropic mechanical, optical and thermal conduction properties.” Carbon 147: 377–384.

[35] Yu, K.-I., et al. (2006). “Synthesis of NiO-embedded carbon nanotubes using corona discharge enhanced chemical vapor deposition.” Diamond and Related Materials 15(9): 1217–1222.

[36] Noshadi, I., et al. (2016). “Porous carbonaceous solid acids derived from farm animal waste and their use in catalyzing biomass transformation.” Applied Catalysis A: General 513: 19–29.

[37] Yoo, D., et al. (2019). “Porosity control of nanoporous CuO by polymer confinement effect.” Scripta Materialia 162: 58–62.

[38] Lowry, E. and M. Piri (2018). “Effects of chemical and physical heterogeneity on confined phase behavior in nanopores.” Microporous and Mesoporous Materials 263: 53–61.

[39] Toyin Jibowu (2016) A Review on Nanoporous Metals. Front Nanosci Nanotech, Volume 2(4): 165–168 doi: 10.15761/FNN.1000129.

[40] Thommes, M. and K. A. Cychosz (2014). “Physical adsorption characterization of nanoporous materials: progress and challenges.” Adsorption 20(2): 233–250.

[41] Lowry, E. and M. Piri (2018). “Effects of chemical and physical heterogeneity on confined phase behavior in nanopores.” Microporous and Mesoporous Materials 263: 53–61.

[42] Shafeeyan, M. S., et al. (2010). “A review on surface modification of activated carbon for carbon dioxide adsorption.” Journal of Analytical and Applied Pyrolysis 89: 143–151.

[43] Xiaoguang Yang & Shaobin Guo (2020): Comparative analysis of shale pore size characterization methods, Petroleum Science and Technology, DOI: 10.1080/10916466.2020.1780258.

[44] Anovitz, L. M. and D. R. Cole (2015). “Characterization and Analysis of Porosity and Pore Structures.” Reviews in Mineralogy and Geochemistry 80(1): 61–164.

[45] Cychosz, K. A., et al. (2017). “Recent advances in the textural
characterization of hierarchically structured nanoporous materials." Chemical Society Reviews 46(2): 389–414.

[46] Thommes, M., et al. (2015). “Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report).” Pure and Applied Chemistry 87(9–10): 1051–1069.

[47] Stalin Joseph, Gopalan Saianand, Mercy R. Benzigar, Kavitha Ramadass, Gurwinder Singh, Anantha-Iyengar Gopalan, Jae Hun Yang, Toshiyuki Mori, Ala’H. Al-Muhtaseb, Jiabao Yi, Ajayan Vinu. Recent Advances in Functionalyzed Nanoporous Carbons Derived from Waste Resources and Their Applications in Energy and Environment. Advanced Sustainable Systems. (2020) 2000169 10.1002/adsu.202000169

[48] Zhou, J., et al. (2019). CHAPTER 1 Carbon-based CO2 Adsorbents. Post-combustion Carbon Dioxide Capture Materials, The Royal Society of Chemistry: 1–75.

[49] Bedia, J., et al. (2020). “Review on Activated Carbons by Chemical Activation with FeCl3.” C 6(2).

[50] Gras, R., et al. (2006). “Template synthesis of carbon nanotubes from porous alumina matrix on silicon.” Microelectronic Engineering 83(11): 2432–2436.

[51] Hwang, S., et al. (2007). “Template-directed synthesis of highly ordered nanoporous graphitic carbon nitride through polymerization of cyanamide.” Applied Surface Science 253(13): 5656–5659.

[52] Zhang, L. and M. Jaroniec (2020). “Strategies for development of nanoporous materials with 2D building units.” Chemical Society Reviews 49 (16): 6039–6055.

[53] Guo, D., et al. (2019). “Facile synthesis of nitrogen-enriched nanoporous carbon materials for high-performance supercapacitors.” Journal of Colloid and Interface Science 538: 199–208

[54] Au - Sterczyńska, A., et al. (2019). “Surface Properties of Synthesized Nanoporous Carbon and Silica Matrices.” JoVE(145): e58395.

[55] Liu, W., et al. (2020). “Preparation and characterization of ordered mesoporous carbon based on soybean oil.” Journal of Materials Science 55(15): 6525–6536.

[56] Fan, J., et al. (2007). “Hard-templating synthesis of a novel rod-like nanoporous calcium phosphate bioceramics and their capacity as antibiotic carriers.” Materials Chemistry and Physics 103(2): 489–493.

[57] Freitas, J. V., et al. (2019). “Coconut shell activated carbon as an alternative adsorbent of inhibitors from lignocellulosic biomass pretreatment.” Industrial Crops and Products 137: 16–23.

[58] Rodriguez-Reinoso, F. and J. Silvestre-Albero (2016). Activated Carbon and Adsorption. Reference Module in Materials Science and Materials Engineering, Elsevier.

[59] Li, B., et al. (2020). “Adsorptive removal and mechanism of monocyclic aromatics by activated carbons from water: Effects of structure and surface chemistry.” Colloids and Surfaces A: Physicochemical and Engineering Aspects 605: 125346.

[60] Kim, Y. I., et al. (2019). “High-capacitance activated bio-carbons with controlled pore size distribution for sustainable energy storage.” Journal of Power Sources 438: 226969.

[61] Lütke, S. F., et al. (2019). “Preparation of activated carbon from black wattle bark waste and its application for phenol adsorption.” Journal of Environmental Chemical Engineering 7(5): 103396.