

Tutorial

How Activated Carbon Can Help You—Processes, Properties and Technological Applications

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Abstract: Activated carbon has many potential applications in both the liquid and gas phases. How activated carbon can help practitioners in industry is explained. This practical teaching article introduces the first part of the special issue on Recent Advances in Applied Activated Carbon Research by providing a handbook explaining the basic applications, technologies, processes, methods and material characteristics to readers from different backgrounds. The aim is to improve the knowledge and understanding of the subject of activated carbon for non-adsorption experts such as professionals in industry. Therefore, it is written in a comprehensible manner and dispenses with detailed explanations to complex processes and many background references. This handbook does not claim to be complete and concentrates only on the areas that are of practical relevance for most activated carbon applications. Activated carbon and its activation and reactivation are initially explained. Adsorption and relevant processes are outlined. The mechanical, chemical and adsorption properties of activated carbon are explained. The heart of the handbook outlines key application technologies. Other carbonaceous adsorbents are only introduced briefly. The content of the second part of the special issue is highlighted at the end.

Keywords: activation; adsorber design; adsorption isotherm; adsorption test; density; hardness; per- and polyfluorinated alkyl compounds; reactivation; thermodynamics; water content



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1. Overview of the Structure of this Tutorial

This tutorial structure is as follows: **Section 2**, **Section 3**, **Section 4**, **Section 5** and **Section 6** have an introductory character. Therefore, **Section 2** on Activated Carbon explains basic terminology in the subsections Definition (2.1), Chemical Structure (2.2), Raw Materials and their Processing (2.3), Activation (2.4), and Regeneration (2.5). This is followed by **Section 3** on Adsorption, Processes and Technologies, which is concerned with process technology concepts in the subsections Introduction to Adsorption (3.1), Basic Concepts of Adsorption (3.2), Thermodynamics of Adsorption (3.3), Adsorption Kinetics (3.4), Dynamics of Adsorption (3.5), Furnace Types and Requirements (3.6), and Activation Level (3.7). The Characterization of Mechanical Properties of Activated Carbon is performed in **Section 4** comprising the subsections Determination of Grain Size Distribution (4.1), Determination of Density (4.2), Determination of Hardness (4.3), Flow Resistance (4.4), and Intergranular Volume (4.5). Furthermore, the Characterization of Chemical Properties of Activated Carbon in **Section 5** is explained in the subsections Water Content (5.1), Ash Content (5.2), Soluble Components (5.3), Volatile Components (5.4), and pH of Aqueous

Extract (5.5). The introductory sections are concluded by the Characterization of the Adsorption Properties of Activated Carbon (**Section 6**) detailing the Adsorption Isotherm for Gases and Vapors (6.1), Adsorption Test for Liquids (6.2), and Performance Testing (6.3).

Section 7 on the Application of Activated Carbon in Practice is the heart of the tutorial with great relevance for application technologists in industry. The corresponding subsections are Areas of Application (7.1), Example Substances and Their Absorbability (7.2), Per- and Polyfluorinated Alkyl Compounds (7.3), Checklist for the Design of Adsorbers (7.4), Drinking Water Treatment (7.5), Swimming Pool Water Treatment (7.6), Car Wash Wastewater Treatment (7.7), Gas Phase: Errors in Adsorbers (7.8), Desulfurization of Natural Gas (7.9) and Catalysts Based on Activated Carbon (7.10).

The tutorial is rounded-up by giving a brief overview concerning Other Carbonaceous Adsorbents in **Section 8**. Corresponding subsections are Activated coke (8.1), Carbon-Based Selective Catalytic Reduction and Overview of Test Methods (8.1.2), Biochar (8.2), and Carbon Molecular Sieve (8.3).

Finally, **Section 9** on Conclusions and Second Part of the Special Issue summarizes the take-away messages and briefly outlines the structure of the special issue. References provided are only essential ones.

2. Activated Carbon

2.1. Definitions

Activated carbon is the name for an adsorbent whose main component is carbon [1]. For this introductory handbook, the author proposes the following definition: Activated carbons are manufactured carbonaceous products that have a porous structure and a large inner surface area. They can adsorb a wide range of substances by holding molecules on their inner surface.

The activated carbon processing of char creates chemical reactions that rearrange its carbon atoms to form a very high number of tiny pores, which create a huge surface area. This high degree of microporosity allows it to adsorb a wide range of molecules [2,3].

The pore volume of most activated carbon products is generally greater than 0.2 mL/g. The internal surface area is greater than 400 m²/g. The pore size ranges from 0.3 to a few thousand nanometers.

In addition, activated carbon can be divided into three different types: powdered carbon, granules and molded carbon. Activated carbon has an outer surface that is limited by the particle size and an inner surface that is determined by the pore structure [4–6]. The distinction is commonly made in four different pore size ranges according to Table 1.

Table 1. Classification of common pore ranges of activated carbon [7].

Pore Class	Pore Diameter (nm)	Sections with Further Information
Submicropores	<0.4	Section 7.10
Micropores	<2.0	Sections 3.6, 3.7, 4.2.5, 6.1.2, 7.10, 8.1 and 8.1.2
Mesopores	2.0–50	Sections 6.1.2 and 8.1.2
Macropores	>50	Sections 3.7, 4.2.3, 4.2.4, 8.1 and 8.1.2

With this classification (Table 1), the submicropores form the smallest pores of an activated carbon particle, with a pore diameter of <0.4 nm. This is followed by the micropores, which have a pore size of <2 nm. The ranges in terms of pore diameter for these two pore classes overlap.

Most adsorbents have a wide pore radius distribution with various maxima. The macro- and mesopores mainly serve the transport processes, whereas the adsorption mainly takes place in the micropores [2,4–6].

2.2. Chemical Structure

The pore structure created in the activated carbon and its properties therefore depend primarily on the raw material and the manufacturing process [2,3]. The basic chemical

structure of activated carbon is very close to that of pure graphite. The graphite crystal consists of layers of fused hexagons held together by weak van der Waals forces (Figure 1).

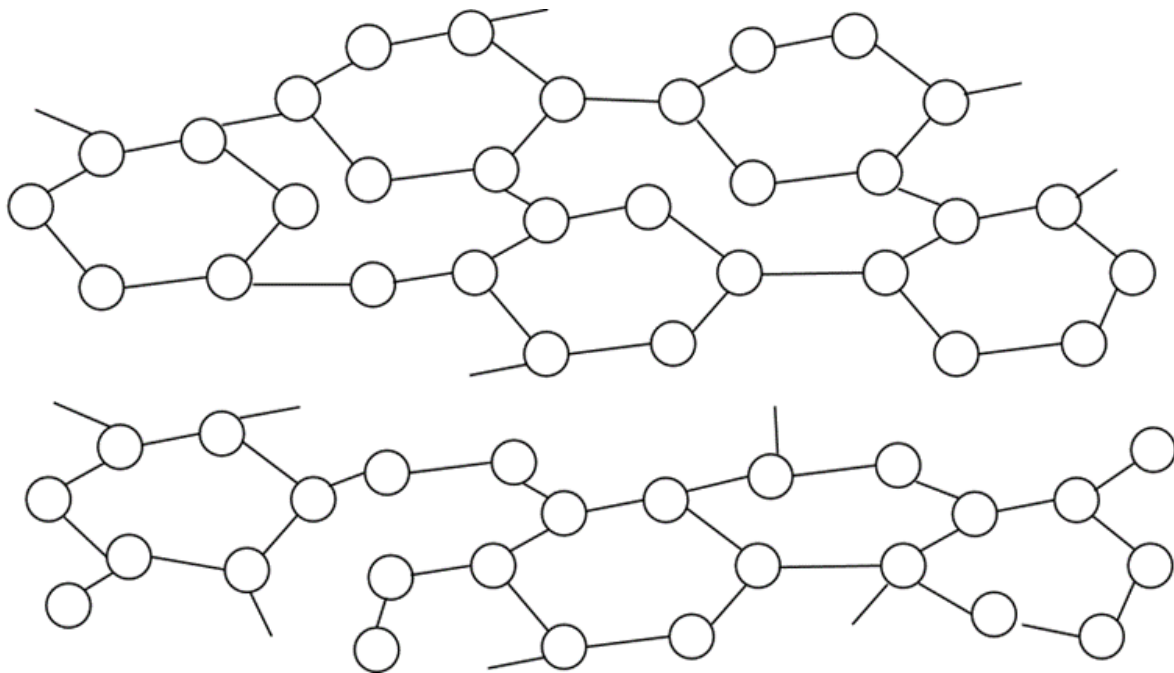


Figure 1. Simplified representation of common activated carbon structures.

Van der Waals forces are the relatively weak non-covalent (covalent = atomic bond or electron pair bond) interactions between atoms or molecules that are generated by various types of dipole forces. The layers are held together by carbon–carbon bonds. Activated carbon is a disordered form of graphite due to the impurities and the manufacturing method (activation process).

Furthermore, biomass-derived activated carbons are honeycomb shaped and possess more aliphatic versus aromatic carbon–carbon bonds. Section 8.2 is concerned with biochar.

2.3. Raw Materials and Their Processing

Activated carbon can be made from a wide variety of raw materials [1]. The most important requirement is that the raw material has a high carbon content. Other parameters such as ash content [8] and trace impurities also play an important role, as they can remain in the end product and affect its properties [2,3].

Table 2 shows the composition of example raw materials to produce activated carbon. The most used raw materials are coal (bituminous, bituminous, anthracite and lignite), coconut shells, wood (softwood and hardwood), peat, polymer resins and fibers. However, coal and peat are classified as non-sustainable commodities. Many other raw materials were also classified as suitable, such as (wal)nut shells as well as olive and palm kernels. However, their commercial applicability inevitably depends on the supply of raw materials. The way in which the selected raw material is manufactured determines the future properties of the activated carbon. Furthermore, the raw material affects the pore structure and the purity of the end product [4–6].

Table 2. Typical compositions of raw materials to produce activated carbon [7,9].

Raw Material	Carbon (C, %)	Hydrogen (H, %)	Oxygen (O, %)	H/C	O/C
Coal	75–97	2–5.5	2–16	0.2–0.9	0.02–0.2
Brown coal	63–70	4–6.5	20–27	0.7–1.2	0.3–0.5
Peat	58–60	5.5–6	33–35	1.1–1.3	0.4–0.6
Wood	48–50	5.5–6.5	43–45	1.3–1.6	0.6–0.7
Nut shells/fruit kernels	45–50	6–6.5	42–46	1.5–1.7	0.6–0.8

The following techniques are commonly used for processing raw materials:

- Flotation: separation of coarse ash.
- Acid washing: removal of ash.
- Grinding: enlargement of the surface.
- Oxidation: prevention of caking and puffing.
- Briquetting: improved handling.
- Carbonation: reduction of volatile components.

However, not every raw material requires the use of every technique.

2.4. Activation

2.4.1. Chemical Activation

Activated charcoal cannot be degraded in nature and must therefore be produced from carbon-containing raw materials such as wood, peat, charcoal, hard coal and nut shells [1]. The higher the carbon content in the starting material, the cheaper it is to produce the activated carbon in general. However, the cost of raw materials varies world-wide. The manufacturing refinement process is also called activation and can take place via chemical activation as well as gas activation, which reflect the two basic principles of activated carbon production [2,3].

Chemical activation is used when shorter batch times and/or lower temperatures are required. A characteristic of chemical activation is that an uncharred plant material is mixed with a dehydrating and oxidizing chemical and then heated to 300 to 1100 °C in the absence of air (pyrolysis). This causes hydrogen and oxygen atoms to be removed from the material by the dehydrating atmosphere and activation and carbonization to take place at the same time [2].

A rotary kiln is usually used as the reactor (Section 3.6). The pore structure and the pore volume are controlled via the ratio of raw material and activation chemical, as well as via the activation temperature [4–6].

The activation chemicals used include phosphoric acid, potassium hydroxide, sodium carbonate, zinc chloride and sodium sulphate. In this process, the product must be washed with water at the end to rid it of the residues of the activation chemicals, resulting in large amounts of wastewater.

2.4.2. Gas Activation

In gas activation, the carbon source is pyrolyzed in an oxygen-free atmosphere at 500–900 °C. This provides an activated coke product (Section 8.1).

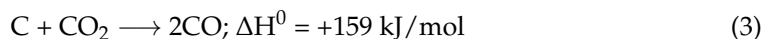
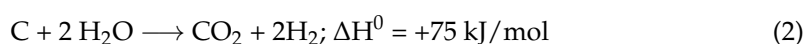
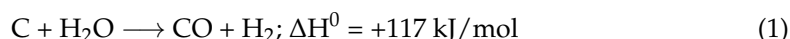
Gas activation is mainly used to produce shaped activated carbon and activated carbon granules [3]. A characteristic of this process is that a carbon-containing raw material is used to produce a shaped body, which is then activated by partial gasification with steam or carbon dioxide at 800–1200 °C. Carbon dioxide, water vapor and oxygen are used as activation media.

Partial gasification ensures that the inner surface is significantly increased. The weight loss that occurs during this process is referred to as the degree of activation or burn-off.

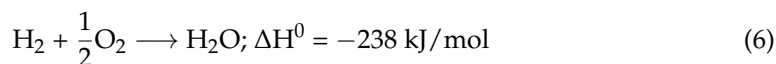
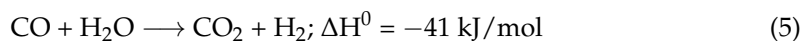
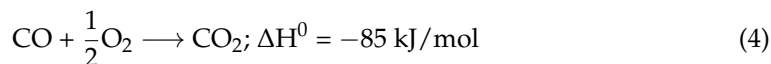
The activation process removes the volatile components and exposes the individual layers of carbon. This forms the pore structure. As more carbon (higher activated) is removed, the internal surface area and pore volume increases [2,4–6].

Key reaction equations are summarized by Equations (1)–(7). The most important reaction is the endothermic reaction of water vapor with carbon (Equation (1)). In chemistry, reactions in which energy must be supplied are called endothermic. The standard enthalpy difference ΔH^0 is positive. The reverse process would be exothermic, releasing energy. Here, the standard enthalpy difference ΔH^0 is negative.

Furthermore, carbon dioxide also reacts with carbon (Equation (3)). The corresponding reaction equations (Equations (1) and (3)) are shown below.

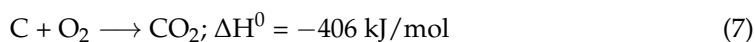


The partial gasification of carbon occurs mainly through the reaction with water vapor. The problem is that the resulting product gases (H_2 and CO) strongly inhibit the gasification reactions (Equations (1) and (3)), since they attach themselves to the active centers of the coal and thus make them inaccessible for the reaction. In addition, heat must be supplied to the reactor since gasification involves endothermic reactions. This heat can be generated by burning the product gases through targeted air metering (Equations (4) and (6)):



The heat balance of the activation process is improved by the released heat of reaction. In addition, the concentration of the inhibiting product gases H_2 and CO is reduced.

The activation temperature can be controlled by the volume of air to be dosed, and the H_2O and CO_2 compounds are constantly re-formed as a result. An undesired side reaction is the combustion of the carbon (Equation (7)), since this does not contribute to the development of porosity. Therefore, it is important to ensure that there is no excess oxygen in the activation process.



The reaction equations listed here are the main reactions with the component carbon. As already mentioned in Section 2.3, the raw material consists mainly of carbon but also of other organic and inorganic compounds. These components also have their own reaction equations, making it beyond the scope of this teaching handbook to consider the entire process.

Several processes are known to produce activated carbon granules and shaped parts; these processes contain the following common process steps:

- Drying and carbonization;
- Activation with water vapor and carbon dioxide;
- Crushing (in the case of granules), sieving and packaging.

In the case of activated carbon pellets, the following additional steps are performed:

- Grinding of the carbonaceous base material;

- Mixing with a suitable binder;
- Extrusion to produce cylindrical shapes or briquetting to produce larger shapes.

The activation step is technically carried out in various reactors, with multi-stage furnaces, rotary kilns, shaft furnaces or multi-stage fluidized bed reactors predominantly being used (Section 3.6). With the selected manufacturing process and the selected starting material, different types of activated carbon can be produced.

2.5. Regeneration

One of the most important properties of activated carbon is its ability to regenerate, i.e., the adsorbed substance is removed from the activated carbon to use it again [1–3]. This is carried out with the process of desorption, by reducing the pressure or increasing the temperature. However, complete desorption of a substance from the inner surface is only possible with difficulty, since the heat of desorption is greatest with small loads. Because of this, a higher temperature is required the more completely a substance is to be desorbed.

In addition, the problem can arise that the desorption temperature rises above the decomposition temperature of the compound in the process. As a result, a residual load consisting of pyrolysis products and carbon deposits remains in the active centers after desorption, which reduces the adsorption capacity of the carbon.

This residual loading can, under reactivating conditions (e.g., the reaction with steam at 700–900 °C), be removed. The impurity is first charred and gasified according to the reaction equations (Section 2.4.2). The process described takes place under the conditions of thermal activation of activated carbon, so this process is referred to as reactivation.

The reaction conditions must be adapted to the reactivity of the activated carbon so that the structure of the carbon is damaged as little as possible. The contamination has a positive effect if its reactivity with water vapor is higher than that of the activated carbon. This makes it easier to gasify the contaminants without damaging the framework and reducing the internal surface area. In addition, undesirable activated carbon losses are avoided.

The sub-steps in the thermal reactivation of activated carbon can be divided into drying, desorption/pyrolysis, gasification of the residual charge, and cooling. The residence time depends on the type of activated carbon and its impurities.

The ignition temperature (also ignition point) of a substance is the temperature to which a substance (or a contact surface) must be heated so that a combustible substance ignites itself in the presence of oxygen solely due to its temperature (i.e., without an ignition source). This ignition point is different for each substance and in some cases also strongly dependent on the pressure.

In addition to thermal reactivation, biological reactivation is also known in water purification. Unwanted materials on the activated carbon are decomposed by organisms. Biological reactivation can often only occur if the compounds are first desorbed, as many microbes cannot enter small pores and crevices. Moreover, this process is difficult to control in practice. The fewer variables involved in the process, the more successful the biological regeneration should be. More information can be found in a recent review paper [10], the content of which is beyond the scope of this handbook.

3. Adsorption and Processes

3.1. Introduction to Adsorption

The accumulation of molecules at the interface of neighboring phases is generally referred to as sorption. If the attachment only takes place on the surface, this process is referred to as adsorption. One of the phases consists of a porous solid (e.g., activated carbon and zeolite) with so-called active centers on its surface. Adsorption is preferably possible in these centers. This makes it easy to separate the smallest amounts from a gas or a liquid using this process [2,3].

3.2. Basic Concepts of Adsorption

For a better understanding of adsorption, the following definitions have become established in adsorption technology and are subsequently used in this handbook [2,3].

Adsorption: The attachment of a molecule from a gaseous or liquid phase to a solid.

Desorption: The removal of a molecule from a solid into the fluid phase (=reversal of adsorption).

Adsorbent: Solid that binds the molecule to be adsorbed.

Adsorptive: A molecule to be adsorbed that is in the fluid phase.

Adsorbed: Molecule bound to the adsorbent.

Adsorbate: Complex of adsorbent and adsorbed.

3.3. Thermodynamics of Adsorption

In the illustration of thermodynamic equilibria, no distinction is made between liquid-phase and gas-phase processes since both use similar model concepts and identical equations. In this way, a unified view is pursued that emphasizes the similarities. In general, the thermodynamic equilibrium describes a state of equilibrium that an adsorption system strives for and therefore represents the drive for the adsorption process.

There are three different possibilities for representing thermodynamic equilibria. The adsorption isotherm describes the relationship between the adsorbed volume (loading of the adsorbent) and the partial pressure of the adsorbent in the gas phase or the concentration in the liquid phase at constant temperatures (=isotherm).

In the adsorption isostere, the adsorbed volume is kept constant (=isostere). This represents the pressure as a function of the temperature at constant loads, which makes it possible to determine the adsorption enthalpies. The process of adsorption can be viewed as a chemical reaction, with the heat released being called the adsorption enthalpy.

The relationship between loading and temperature at constant pressure (=isobar) can be shown in an adsorption isobar. However, the usual representation is via the adsorption isotherm, which is also called the equilibrium isotherm. Understanding the loading as a function of the concentration or the partial pressure is important for the quantitative description of adsorption processes.

3.4. Adsorption Kinetics

The kinetics of an adsorption process describe how quickly a state of equilibrium (thermodynamics) is established between the adsorbate and the adsorbent, depending on the adsorption processes. In general, the mass transport within an adsorption process can be divided into four steps: convective or diffusive transport in the fluid phase, mass transport through the boundary layer surrounding the particles, mass transport in the pores of the adsorbent, and adsorption [2].

The first step, which is the convective or diffusive transport in the fluid phase, is not attributed to the kinetics of adsorption. During adsorption, the adsorption enthalpy is released, which in turn is dissipated to the fluid phase. This process is subject to the transport kinetics of heat, which consists of the following sub-steps: energy transport in the adsorbent, energy transport through the boundary layer surrounding the particles and convective or diffusive heat transport to the fluid phase.

In the liquid phase, the heat transport can usually be neglected due to the high heat capacity of the surrounding liquid, whereas it is of considerable importance in the gas phase adsorption. There are no serious differences in mass transport, since there are processes in both states of aggregation that are limited in transport [3].

The mass transport kinetics are usually dominated by the mass transport in the pores. Five different mechanisms take place here, sometimes in parallel or one after the other. These mechanisms are mentioned below.

- Drying and carbonization;
- Viscous flow (only in the gas phase);
- Knudsen diffusion (only in the gas phase) [11];

- Free pore diffusion (gas and liquid phase);
- Surface diffusion (gas and liquid phase);
- Intergranular diffusion (gas and liquid phase).

3.5. Dynamics of Adsorption

3.5.1. Process Dynamics

The interaction of thermodynamics and kinetics results in typical process dynamics for adsorption systems. This dynamic is visible to the plant operator in the form of breakthrough curves with gases such as nitrogen and methane. The dynamics are of practical importance, among other things, in the regulation, clock reversal and in the design of the adsorbers [2,3].

Breakthrough curves describe the course of the concentration of a substance at the outlet of an adsorber as a function of time. With isothermal operation and a constant inlet concentration, the adsorber can be divided into three zones [12].

In the simplest case (isotherm; Section 3.3), a concentration (partial pressure) and loading front migrates through the adsorber. Based on the profile that occurs, the adsorber is divided into three zones: equilibrium zone, mass transfer zone and another equilibrium zone. The adsorbent (e.g., activated carbon) is unloaded in the first equilibrium zone. According to the equilibrium isotherm, the partial pressure of the adsorptive in the gas phase is also zero. At the beginning of the process, this zone occupies the entire adsorber. At the end of the adsorption, it has completely disappeared [12].

During adsorption, the mass transfer zone migrates through the adsorber and displaces the equilibrium zone. The adsorption process takes place exclusively in this zone. The curvature of the fronts is essentially determined by the isotherm shape (Section 3.5.1) and the kinetics (Section 3.5.2).

According to the isotherm equation, the adsorbent is fully loaded in the second equilibrium zone. The partial pressure of the adsorbent in the gas phase corresponds to the value of the raw gas entering the adsorber. At the end of the process, this zone occupies the complete adsorber [7,12].

The ideal case described here is usually not encountered in real adsorbers. The classical profile only appears after a certain start-up time and distance. As a rule, the profile changes considerably during adsorption; depending on the boundary conditions, it becomes steeper or flatter. A stable profile only sets in when the ascending and descending effects are balanced.

3.5.2. Influence of Thermodynamics

The migration speed of the concentration front can be derived from the equilibrium theory. There, the speed depends on the reciprocal slope of the isotherm, so the speed decreases when the isotherm becomes steeper.

The higher concentration migrates more slowly through the fixed bed than the lower concentration, resulting in a flattening of the breakthrough curve. The opposite case would be a decreasing isotherm slope. The migration speed of the high concentration increases compared with the low concentration. This steepens the breakthrough curve.

3.5.3. Influence of Kinetics

In addition to thermodynamics, the kinetics also have a significant influence on the shape of the breakthrough curves. With increasing inhibition of mass transport (=small diffusion or mass transfer coefficient), the mass transfer zone widens; that is, the fronts become flatter. The diffusion and mass transfer coefficients are a measure of the mass transfer of the molecule from the fluid phase to the surface of the adsorbent. In the opposite case of instantaneous equilibration (i.e., infinitely fast kinetics), a sharp rectangular profile is obtained.

3.6. Furnace Types and Requirements

The most important requirements for the furnace technology are high temperature, good mass transfer and good control of the reaction gas [13]. The following kiln types have proven their worth in technical applications according to CarboTech (Essen, Germany) and the literature [7,13]: deck kilns, shaft kilns, rotary kilns and fluidized bed kilns. The residence time for all cookers generally depends on the number of trays and the allocation. The reaction rate rests on the temperature and the concentration of the activation media (water vapor and carbon dioxide). The residence time in the deck oven depends also on the height. In the case of the rotary kiln, the residence time is a function of the incline, the internals such as weirs and the rotational speed. Good heat and mass transport, a narrow residence time spectrum and a short residence time leads to more micropores in the fluidized bed furnace.

3.7. Activation Level

The degree of activation determines the properties of the activated carbon. The bulk density, the macropore volume, the impact hardness, the micropore volume, the mean adsorption pore diameter and the Brunauer, Emmet and Teller (BET) surface area (Section 6.1.1) depend on the degree of activation [14].

4. Characterization of Mechanical Properties of Activated Carbon

4.1. Determination of Grain Size Distribution

The mechanical properties are important for producers, suppliers and customers of different activated carbon products. The methods specified for the characterization are not necessarily all carried out in the same way. Sieve analyses serve to determine the particle size distribution and are usually carried out with sieve machines. The screening machine consists of a set of graded standardized screens with a bottom plate and a cover. For analysis, based on the International Organization for Standardization ISO 2591-1:1988 [15], the bulk material is kept in oscillating motion for a defined time.

Additional tapping devices can lead to a falsification of the analysis due to the abrasion of activated carbon. The particle size distribution is given in percentages by mass. When naming the grain boundaries, usually 5% undersize and oversize are tolerated. However, the sum must not exceed ten percent by mass.

Further grain description is important. Therefore, in addition to the grain distribution, the grain diameter and grain length are also determined.

4.2. Determination of Density

4.2.1. Bulk Density

The bulk density is understood to mean the mass of a unit volume of loosely filled material. The indication of the filling density is important for the dimensioning of containers for activated carbon manipulation. It is determined in a simple manner by weighing a loose bed in a defined volume [7].

4.2.2. Pour Density

The bulk density indicates the density of a defined bed. Reproduction requires the use of standardized devices. The standard test method for activated carbon apparent density is found in American Society for Testing and Materials (ASTM) D 2854 [16].

In the testing device, activated carbon is filled into a measuring cylinder via a vibrating channel. A bulk material is produced according to the standard and the bulk density is determined.

4.2.3. Tapped Density

The coal heap compacted under defined conditions is characterized by the vibration density. For activated carbon, the use of a ramming volumeter according to the German Industrial Standard (DIN) EN ISO 787-11 [17] has proven itself. For better reproducibility,

the tapped density is given with reference to the dry substance. For this purpose, the sample is either dried beforehand or the moisture content of the sample is considered in the calculation.

4.2.4. Apparent Density (Mercury Density)

The apparent density, also known as mercury density, is the mass per volume of a single activated carbon granule including its pore system. Mercury is used for the determination, which completely fills the space between the grains of an activated carbon bed. The measurement is carried out without pressure and neglecting the error that mercury fills small parts of the macropores ($>7\text{ }\mu\text{m}$). Values obtained with this measuring method vary between 0.6 and 0.8 g/cm^3 for activated carbon. The apparent density can also be calculated from the tapped density and the intergranular volume [7].

4.2.5. True Density (Helium Density)

The true density, also known as helium density, is the mass per volume of the pure carbon framework of the activated carbon. The determination is carried out using a pycnometric method with pore-penetrating gases or liquids whose molecules are small enough to completely penetrate the micropores. The pycnometer is a measuring device for determining the density of solids or liquids by weighing [9].

Depending on the gas to be measured, a distinction is made between helium density and methanol density. The measurement with helium is more accurate because it penetrates deeper into the pores. The true densities of commercially available activated carbon are around $2.0\text{--}2.1\text{ g/m}^3$ [9].

4.3. Determination of Hardness

4.3.1. Mechanical Resistance

There are several test methods for determining the hardness of an activated carbon sample, three of which are discussed in more detail. These simulate different types of stress and therefore result in different hardness values that cannot be transferred.

For impact hardness, a charcoal sample (10 mL) is filled into a standardized steel tube. The filling is loaded with 10 impacts with a built-in drop stamp. After every two impacts, the carbon filling is sieved off by hand using a 0.5 mm sieve before the next load. A 0.25 mm sieve is used for fine-grained activates. The sieve residue after 10 impacts is given as a percentage of the weight as a measure of the impact hardness [7].

4.3.2. Abrasion Hardness

For abrasion hardness, a mechanical load is applied to the activated carbon using a vibratory mill (crushing machine). The undersize fraction of the activated carbon sample is first screened out. Then, 100 g of the sample is put into a grinding vessel and ground in the vibratory mill for 30 min . Particles smaller than 0.5 mm are then screened out and the proportion of particles larger than 0.5 mm gives the abrasion hardness in percent [7].

In addition to testing using a vibratory mill, there are other test methods for determining abrasion hardness, such as stirring abrasion hardness, ball abrasion hardness and rolling abrasion hardness. These methods are not covered further in this guide.

4.3.3. Ballpoint Pen Hardness

The abrasion hardness measurement according to ASTM D3802 [18] is referred to as the Ro-Tap hardness (known as ballpoint pen hardness in English). Here, a specific activated carbon fraction is subjected to a shaking and hitting load. The values determined are very high (typically $> 95\%$). This hardness is often specified on data sheets as the standard hardness. However, the informative value for pellets is low.

4.4. Flow Resistance

Various approaches and calculation rules are available for calculating the flow resistance of a particle bed. The Ergun equation [19] is suitable for activated carbon fills, where the pressure loss (resistance) can be calculated as follows (Equation (8)) given knowledge of the intergranular volume (compare with Section 4.5) and the particle size:

$$\frac{\Delta P}{L} = 150 \times \frac{(1 - \varepsilon)^2}{\varepsilon^3} \times \frac{\eta \times w}{d^2} + 1.75 \times \frac{(1 - \varepsilon)}{\varepsilon^3} \times \frac{\rho \times w^2}{d_{\text{mittel}}} \quad (8)$$

where:

- ΔP = pressure drop (dyn/cm²);
- L = length or height of the (filled) bed (cm);
- ε = intergranular volume (cm³);
- η = dynamic viscosity (poise); 1 poise = 1 dyn × sec/cm²;
- w = flow velocity (cm/sec);
- d = particle diameter (cm);
- ρ = density of the liquid (grams/cm³);
- d_{mittel} = average particle diameter (cm).

4.5. Intergranular Volume

The intergranular volume describes the cavity or gap volume between the individual particles in a bed. For the determination, an activated carbon bed of 200 mL is prepared by bumping and tapping until the filling level is constant in a measuring cylinder. This quantity is heated with deionized water until all bubbling stops. After cooling, the adhering water is centrifuged in a laboratory centrifuge until no more water can be observed draining off. The sample is backfilled tightly, and the interstices volume is measured by adding water from a burette [7].

Another possibility of determination is the calculation of the intergranular volume. To undertake this, the vibration and apparent density must be known. The volume can then be calculated by Equation (9) [7].

$$\varepsilon = 1 - \rho_{\text{Rüttel}} / D_{\text{Hg}} \quad (9)$$

where:

- ε = intergranular volume or porosity;
- $\rho_{\text{Rüttel}}$ = tap density;
- D_{Hg} = apparent density.

The ratio of the compacted fill to the apparent density indicates the proportion of the fill made of activated carbon. The rest forms the empty space between the activated carbon particles and thus the porosity or the interstitial volume.

5. Characterization of Chemical Properties of Activated Carbon

5.1. Water Content

The simplest method for determining the water content of activated carbon is the drying-oven method. This is based on the ASTM method D2867-9 [20]. The activated charcoal is dried for three hours at 150 °C, and the weight loss is determined by reweighing after cooling in the desiccator for drying purposes.

The temperature of the drying cabinet and the duration of the drying time can vary depending on the type of activated carbon. Very moist activated carbon often requires a longer drying time of up to 24 h. Granular activated carbon also takes more than three hours to reach a constant mass.

The dry box method cannot be used when testing spent (used) activated carbon. These are optionally covered with highly volatile substances or substances that are volatile with steam. In these cases, the Karl Fischer titration method [21] must be performed. This method is based on the quantitative determination of water by titration.

5.2. Ash Content

The ash content of activated carbons is determined using an electric muffle furnace with porcelain crucibles applying the ASTM method D 2866 [8,13]. This is a kiln in which the heat source is separated from the firing chamber by a refractory insert (muffle).

The pre-dried sample is placed in the pre-heated ashing furnace and ashed at 650 °C for at least four hours. In the process, mineral components are converted to the corresponding oxides. The ash content is therefore a measure of the mineral content of an activated carbon, given in percentage by weight. The ash consists mainly of silicon oxide and aluminum oxide. The amount of ash depends on the raw material used. According to the laboratory records of the author and supported by the literature [7,9], typical values are 2–3% by weight for coconut-shell-based activated carbon, 5% by weight for wood-based activated carbon and 8–15% by weight for carbon-based activated carbon.

5.3. Soluble Components

In many areas of application in the liquid phase, the content of soluble components in an activated carbon is of interest. The focus here can be on the solubility in neutral water or the proportion of acid-soluble coal by-products. For special applications, the amount of components that can be dissolved in organic solvents can also be important.

To determine the water-soluble components, a precisely weighed amount of dried activated charcoal is boiled under reflux with water for a few minutes, or about an hour for grain charcoal. After the cooled suspension has been filtered, an aliquot portion is evaporated, and the residue is determined gravimetrically. An aliquot is defined as a part that is contained in another as an equal number of times and is calculated as a percentage or proportion of a total [7].

This test method only allows a statement to be made about the total content of foreign substances in an activated carbon. In very many cases, however, certain cations (positively charged ion) or anions (negatively charged ion) are undesirable, so that only a single determination of the interference substance in question allows an exact assessment. For example, a few percent by weight of silicic acid in an activated carbon may not be a problem, whereas even a few parts per million of zinc or lead may be unacceptable in the same application.

5.4. Volatile Components

With loaded activated carbons and sometimes with fresh carbons, the determination of volatile components can be important. Based on BS ISO 562:2010 [22], the sample is annealed in a crucible (with the exclusion of air) for seven minutes at 900 °C in a muffle furnace [13]. The volatile components are stated as percentages by mass based on the dry starting substance.

5.5. pH of Aqueous Extract

Activated carbon can have a major impact on the pH value due to its mineral content and the presence of surface oxides in aqueous systems. Since pH-value-sensitive substances can be treated with activated carbon in the chemical and food industry, determining the pH value is often an important criterion for the suitability of an activated carbon. For this purpose, the activated carbon (ground) is boiled with deionized water in a beaker for about five minutes and left to cool and allow the activated carbon to settle. The supernatant liquid is then decanted, and the pH value is determined using a glass electrode. This method was developed by CarboTech (Essen, Germany) laboratories for the provision of values for the activated carbon product sheets [7].

5.6. Elemental Composition

X-ray fluorescence (XRF) spectroscopy analysis is an analytical method based on X-ray fluorescence. It is used in the qualitative and quantitative determination of the elementary composition of a substance sample, since this is not destroyed by the measurement and no

breakdowns are required. Inductively coupled plasma mass spectrometry (ICP-MS) is a robust but also very sensitive mass spectrometric analysis method in inorganic analysis for trace element analysis, especially for heavy metals [7].

6. Characterization of the Adsorption Properties of Activated Carbon

6.1. Adsorption Isotherm for Gases and Vapors

6.1.1. Determination of the Specific Surface (BET Method)

The determination of an adsorption isotherm (Section 3.3) of a specific substance is of practical interest for the assessment of an activated carbon that is to be used, for example, for solvent recovery. The evaluation of adsorption isotherms for deriving the specific surface area and pore distribution of activated carbon is of great theoretical importance. In addition, isotherms of certain substances (e.g., benzene or carbon tetrachloride (CTC)) are used for the comparative evaluation of gas adsorption carbons [7].

The specific or internal surface area is generally understood to mean the surface area of a solid body in relation to the mass. This surface is created by the walls of the numerous pores in the activated carbon. As a result, the inner surface is many times higher than the outer surface of an adsorbent grain. For example, a few grams of activated carbon can have an internal surface area the size of a soccer field (approx. 1500 m²).

The actual adsorption processes take place at the specific surface. The assessment of the adsorption performance of an adsorbent should not be based solely on its inner surface since the adsorption process depends on several parameters. However, a large internal surface area is desirable.

The determination of the specific surface area is based on the determination of the amount of adsorbate or consumed adsorbent required to cover the external surface and the accessible pore surface of a solid with a complete adsorbate monolayer. This means that a layer of individual molecules of the test substance forms on the surface of the activated carbon.

The so-called monolayer capacity can be calculated from the adsorption isotherm using the BET equation [14] according to the German Norm DIN 66132:1975-07 [4]. Nitrogen or noble gases are used as measuring gases. Another measurement method for determining the inner surface is the iodine number (Section 6.2.2).

6.1.2. Determination of the Pore Radius Distribution

An important assessment criterion for an activated carbon sample is its pore radius distribution; that is, the distribution of the total pore volume of this carbon according to the pore size. The measurement of the pore radius distribution is carried out using various measurement methods, which means that the measurement is complex and not carried out by every laboratory. The macro- and mesopores are determined with mercury intrusion (German norm DIN 66133:1993-06 [5]) and nitrogen sorption (DIN 66134:1998-02 [6]), whereas the micropores are measured by adsorption of, e.g., nitrogen, benzene and water vapor.

6.1.3. Benzene Isotherm

In addition to nitrogen, benzene vapor has been used particularly frequently to determine the adsorption isotherms. Benzene's low tendency to form decomposition products and thus cause measurement errors is probably the main reason for its widespread use, although the toxicity of this test substance requires extremely clean work and careful handling.

The work is carried out in practice by mixing air saturated with benzene vapor with clean air in different ratios, thereby setting charging flows of different relative pressures between 0.1 and 0.9. A suitable sample container, which is in a thermostat, is loaded until the weight is constant. The measurement starts with the highest concentration, whereby the desorption isotherm is measured [7].

Due to the toxicity of benzene, comparison measurements can be made with cyclohexane, as this has a similar structure and is less toxic. With the knowledge gained, it is possible to convert cyclohexane isotherms into benzene isotherms.

6.1.4. Carbon Tetrachloride Test

This test is based on the adsorption of carbon tetrachloride (CTC) from the gas phase and determines the pore volume of an activated carbon. Internationally, moldings are sometimes purchased according to the CTC number. The abbreviation CTC is also retained in other languages such as in German.

A gas stream saturated at 0 °C is heated to 25 °C and passed over the activated carbon. The uptake, expressed as a weight percent, is the CTC number.

Due to the toxicity and ozone-depleting potential of carbon tetrachloride, the substance is commonly replaced by butane (ASTM D5742-16 [23]) in the analysis. With the help of a conversion factor (2.55), CTC numbers can still be determined with butane as the test gas (Section 6.1.5).

6.1.5. Butane Activity

Like the method using carbon tetrachloride (CTC) and the iodine number, this method is used to determine the pore volume of an activated carbon. Carbon tetrachloride activity (Section 6.1.4) has been replaced by butane activity (ASTM D5742-16 [23]) due to the ban on carbon tetrachloride. There is a fixed conversion factor of 2.55 between the two activities (CTC activity = $2.55 \times$ butane activity). Butane working capacity means that the adsorbed butane is desorbed again with air.

6.2. Adsorption Test for Liquids

6.2.1. Methylene Blue Adsorption (MB Value)

The adsorption of a single test substance from an aqueous solution cannot be used for a general characterization of the pore distribution of an activated carbon. On the other hand, a comparison of the measurements with different test substances, such as methylene blue or iodine, allows an assessment of activated carbon.

The adsorption of methylene blue provides information about the surface area and the adsorption capacity of an activated carbon. Here, pores larger than 1.5 nm are filled. The so-called methylene blue (MB) value gives an indication of the decolorization performance and the adsorption capacity for larger molecules, which often correlate.

When determining the MB value, a methylene blue standard solution is added to the ground activated carbon. After stirring for 30 min, the suspension is filtered off. Acetic acid is added to a certain amount of the filtrate in a volumetric flask and diluted. The extinction of the dilution is then measured at a wavelength of 620 nm, from which the MB value can be derived. Extinction is a measure of the attenuation of radiation (e.g., light) after it has passed through a medium. It depends on the wavelength of the radiation. This method was developed by the Carbotech (Essen, Germany) laboratories [7].

6.2.2. Iodine Adsorption

Like the MB value (Section 6.2.1), iodine adsorption (also iodine number) is an indication of the available surface area of an activated carbon. Based on ASTM D4607-14(2021), the amount of iodine (I) is given in milligrams per gram (mg/g) of activated carbon (AK) ($\text{mg I}_2/\text{g AK}$).

Coconut activated charcoal is often purchased based on the iodine number. When determining the iodine number using the ASTM D4607-14(2021) standard method [24], it is to be expected that iodine will form a monomolecular layer (Section 6.1.1). As a result, there are connections between the iodine number and the specific surface area (e.g., BET surface area [14]) of an activated carbon.

An adsorber should be replaced if the iodine number (after desorption at 150 °C) is very low. Another reason for replacement is if the activated carbon also has a very high ash content.

6.2.3. Specific Adsorption Isotherms

The general procedure described is a method for evaluating activated carbon using an adsorption isotherm. A sample of activated carbon is brought into contact with the solution to be tested for a specific period. The length of time is selected in such a way that a state of equilibrium was established after the process has ended [7].

An isotherm is graphically created based on the respective concentrations of the test substances in the liquid phase (residual concentration) and the solid phase (load). An example is the determination of a chemical oxygen demand adsorption isotherm for seepage water and other wastewater.

6.3. Performance Testing

In general, performance testing involves the process by which an application is tested to know its current and sometimes also long-term system performance. Such tests check how a system performs in terms of the responsiveness and stability when tested under varying (work)load and boundary conditions.

For example, an activated carbon filter is tested under multiple and different loads as well as boundary conditions. The test engineer checks the time taken by the filter system to respond to different changes in variables. This procedure determines the speed with which the filter works, and it involves subtests that are performed within a lab or pilot plant setup referred to as quantitative tests. Such tests should be similar to those in a production-like industry environment.

7. Application of Activated Carbon in Practice

7.1. Areas of Application

The areas of application for activated carbon in practice are very diverse, both for liquids and gases. Fluid application examples are as follows [1,25]:

- Drinking water production;
- Wastewater treatment (municipal, such as the fourth treatment stage, and industrial);
- Groundwater remediation;
- Landfill leachate;
- Process water treatment;
- Discoloration of liquids;
- Lightening of oils and sugar solutions;
- Pharmaceutical applications;
- Ultrapure water production;
- Gold leaching;
- Material separation;
- Chromatography (analysis; technical (e.g., vitamins and medicines)).

Adsorption processes are used in many areas in which gaseous or vaporous components are to be removed from gas streams or gas mixtures are to be separated. Gas treatment examples are as follows:

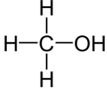
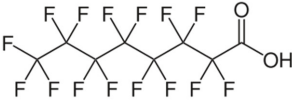
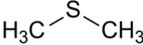
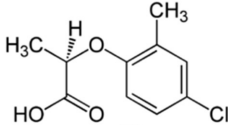
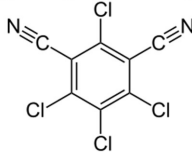
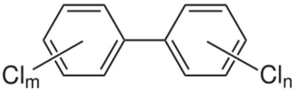
- Adsorptive air separation (oxygen and nitrogen generation);
- Processing of raw gases (e.g., steam reformer and ethylene plants);
- Separation of gas mixtures in refineries (isomer separation);
- Pre-treatment of process air (compressed air and cryogenic air separation); in the cryogenic rectification process, air is cooled down to −195 °C and partially liquefied;
- Exhaust air purification (removal of impurities such as solvents from printers, paint shops and chemical plants);
- Flue gas treatment to reduce pollutants emitted from the burning of fossil fuels;

- Exhaust gas cleaning (removal of mercury, dioxins and furans from waste incineration plants);
- Pollutant and odor filters for rooms and vehicle cabins;
- Landfill gas;
- Biogas applications;
- Military and security technology (gas mask filters and nuclear, biological and chemical (NBC) defense filters in military vehicles).

7.2. Substances and Their Absorbability

Table 3 provides a qualitative overview of example substances and their general absorbability. Further information such as contamination and system design must be considered. Typically, the more chemical interactions that occur between the activated carbon and the chemical compounds, the better the absorbability.

Table 3. Example substances and their absorbability according to the experience of the author [7].

Name	Chemical Composition	Absorbability
Ammonia		None; only possible with impregnation of the activated carbon
Methanol		Not or only a little
Dichloromethane		Little to medium
Perfluorooctanoic acid		Middle
Dimethyl sulfide		Middle
Mecoprop		Good
Chloroethanonil		Good
Polychlorinated biphenyls		Good
Benzene		Good
Toluene		Good
m-Xylene		Good

7.3. Per- and Polyfluorinated Alkyl Compounds

7.3.1. Introduction, Characteristics and Distribution Routes

Per- and polyfluoroalkyl substances (PFASs) are aliphatic organic compounds in which at least one carbon atom has the hydrogen atoms on the carbon skeleton completely replaced by fluorine atoms [25]. The definition of a PFAS was solidified around 2020. Before that, the term perfluorinated surfactants was often used. According to general estimates, there are around 5000 different substances that are classified as PFASs. Two examples of PFAS chemicals are shown in Figure 2.

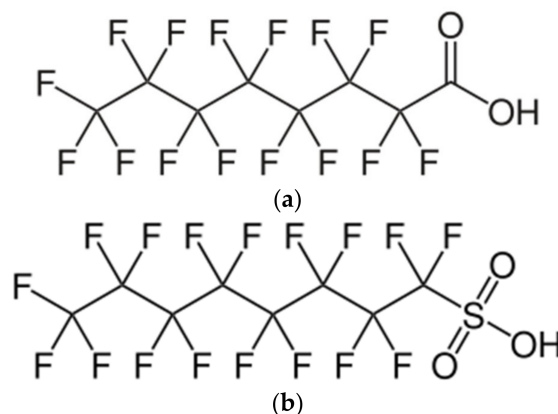


Figure 2. Examples of per- and polyfluoroalkyl substances (PFASs): (a) perfluorocarboxylic acids and (b) perfluorosulfonic acids.

Most PFAS chemicals are completely decomposed at combustion temperatures of around 1500 °C. However, incineration is very energy intensive and suitable incineration plants are rather rare. Some recent references from the literature also report decomposition of some PFASs at more moderate temperatures between 120 and 1000 °C but with residence times of up to one hour. The most prominent properties of PFASs and associated findings are as follows [25]:

- Pollutant and odor filters for vehicle cabins;
- Water repellent;
- Grease resistant;
- Chemically very stable (persistent) and very mobile;
- Use in coatings (pans, paper, cardboard, textile fibers, fire extinguishing agents, metal cleaners, etc.);
- Surfactant (lipophilic chain with hydrophilic group);
- Accumulation in humans, animals and soil;
- Are suspected of causing various illnesses.

Since PFASs or their breakdown products are very persistent in the environment; they are also often referred to as chemicals of perpetuity. Nevertheless, in manufacturing industries, PFASs are favored for their toughness and functional properties, giving many types of products in the home (including skin creams and cosmetics, car and floor polish, dishwasher rinse aids, textile and fabric treatment waterproofing agents, food packaging and popcorn bags for the microwave, baking tins, frying pans as well as outdoor equipment and shoes) non-stick, water-repellent and fat-dissolving properties. Similarly, there are many and widespread uses in industry, especially in fire-fighting foam.

7.3.2. Removal Procedure

This subsection briefly introduces the advantages and disadvantages of the processes for removing per- and polyfluorinated alkyl compounds (PFASs) using activated carbon, ion exchange (anions) and reverse osmosis. Other methods such as nanofiltration, electro-chemical oxidation systems and adsorption with other adsorbents are also possible.

Activated-carbon-based solutions retain PFASs and other micropollutants, such as pesticides and solvents, are easily scalable and do not require complex technical devices [23]. On the other hand, there are significant differences in the reduction of impurity concentrations for the different types of coal (mineral or vegetable). Activated carbon has been associated with rapid saturation (four to eight months) for short-chain PFASs (e.g., perfluorobutanoic acid (PFBA)) but better performance for longer carbon chains (e.g., 13 months for perfluorobutanoic acid (PFOA)). If necessary, pre-filtration is also required.

There is no evidence of saturation or exhaustion associated with the use of activated charcoal. Therefore, regular analyses are required. However, these are difficult and expensive. A significant impact on operating costs and any capital expenditures and/or transportation costs for granular activated carbon are also serious challenges. The distance between the raw material and the manufacturing sites is often critical. Shipping can be a significant cost since yields are typically low.

With ion exchange (anions) processes, PFASs are not primarily removed by ion exchange but, as with activated carbon, via non-polar interactions. Therefore, the long-chain PFASs are better removed than the short-chain ones in the ion exchanger. Ion exchangers retain PFASs and other pollutants such as nitrate. The material can be regenerated on site. However, this also has disadvantages (see below). Another advantage of ion exchangers is the ease of application on a small scale for single use and on medium and large scales for regeneration.

The disadvantages with ion exchangers are as follows: An effective pre-treatment with, for example, sand filtration is required. The regenerative ability is limited. Only a partial regeneration of a PFAS with ten percent by weight of common salt is possible. In addition, the disposal of regeneration solutions is extremely problematic. Process engineers also receive no indication of technology saturation and depletion. Regular analyses are therefore required. These are difficult and expensive. Another disadvantage is the removal of competing ions such as nitrate and sulphate.

Reverse osmosis holds back all PFASs and other pollutants equally. This includes pesticides, solvents, metals, ammonium ions and arsenic. It represents a simple application for small and medium scales. Reverse osmosis is not subject to saturation, and it is easy to monitor for membrane clogging.

The disadvantages of reverse osmosis are the high-water consumption (about 15% of the treated flow rate) and the need for heavy pre-treatment. Mineral salts and trace elements are removed so well that the drinking water needs to be re-mineralized. Reverse osmosis in water treatment has a not inconsiderable impact on operating costs. The disposal of the concentrate is difficult to organize. Reverse osmosis is not able to completely remove the short-chain compounds (e.g., C3). The energy consumption is up to 1.0 kWh/m³ in the case of low-pressure reverse osmosis and considerable in the case of ultrafiltration pre-treatment (0.31–0.36 kWh/m³).

7.4. Checklist for the Design of Adsorbers

7.4.1. Design Information

Batch adsorption experiments are often carried out by adding a known amount of adsorbent (e.g., contaminant) to a liquid solution at a pre-determined initial concentration and following the change of state brought about by the passage of time concerning the concentration of the adsorbate. These experiments are often carried out as the basis for real flow adsorption processes where the adsorption media are stationary and the adsorbent passes through the filter media continuously.

If there are no experimental data from a pilot test by the user (customer), the design of an adsorber is a challenge. The customer's request should be checked for completeness. Initial information about the whole process should be collected through inquiries, e.g., via simple questions such as the following:

- Where does the water to be treated come from?
- Where should it go?

- Have there already been similar cases?
- What is the service life or the capacity?

This information is important for the selection of the activated carbon and for the dimensioning of the filter. The following information is required for the actual design of adsorbers:

- Clear identification of the substance or substances to be adsorbed. Target substances can be individual substances or mixtures. Substances can also be recorded as sum parameters.
- Definition of the medium (e.g., water, gas and organic liquid) from which the substance is to be adsorbed.
- Applications such as processes, environment and intended use of the treated water.
- Concentration of the component to be adsorbed.
- Flow rate.
- General boundary conditions such as temperature and pressure.
- Recovery option.
- Cleaning target (input concentration and target concentration).
- Desired service life.
- Process conditions such as plant availability, safety and downtime.
- Exclusion criteria for activated carbon.

7.4.2. Questionnaires to Request Customer Data

For design purposes, questionnaires are needed to request customer data. The following questionnaire sections are most needed.

Description of the origin of the material flow to be processed

Brief description of the process

Hydraulic conditions:

- Flow rate (minimum, average and maximum);
- Boundary conditions such as temperature, pressure and humidity;
- Oxygen concentration;
- Miscellaneous.

Composition of the components:

- Entry and target concentration;
- Safety data sheets.

Plant operating time:

- Operation mode including continuous or intermittent operation;
- Operating hours per day and year;
- Downtimes (scheduled and potentially unexpected ones).

Installation type:

- Inside the building;
- Outdoor installation on the building roof or next to the building.

Procedural or process flow diagram

Dimensions of the adsorber:

Figure 3 can be used when selecting activated carbon [7]. Basic data for the design are summarized in Table 4. The recommended filtration speeds (m/h) for common liquids are as follows: drinking water (5–15; sometimes up to 20), municipal wastewater (5–12), landfill leachate (0.3–2), process water (10–20) and industrial wastewater (2–15). Indicative values for empty pipe residence times (minutes) are as follows: drinking water (5–20; sometimes up to 30), municipal wastewater (15–40), landfill leachate (40–60), process water (5–40) and industrial wastewater (10–60).

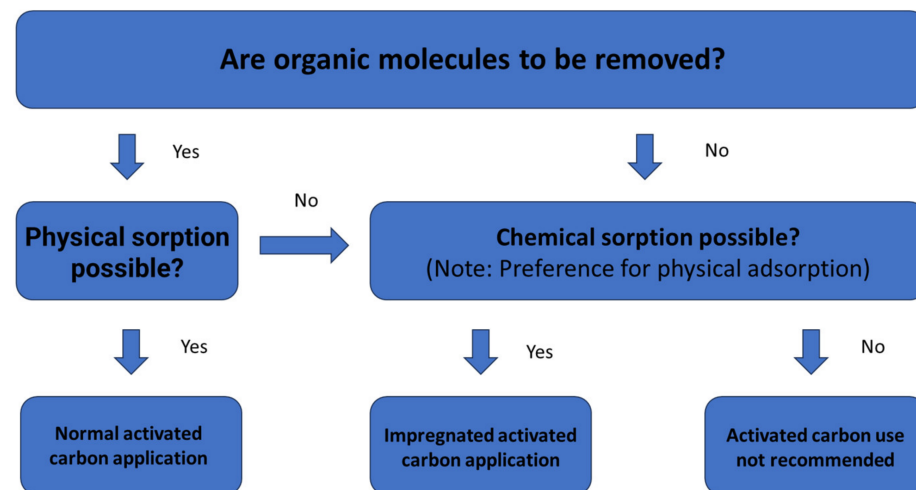


Figure 3. Selection criteria for the activated carbon when removing organic molecules.

Table 4. Basic data for the activated carbon adsorber design according to the experience of the author [7].

Design Parameters	Design Parameters	Liquid Phase
Activated carbon granulation (mm)	3–4	0.5–2.5
Activated carbon layer height (m)	0.5–1.5	2–15
Mass transfer zone (m)	0.005–0.3	0.5–5
Flow rate (cm/s)	10–50	0.03–0.7
Contact time (s)	2–3	1800–3600
Activated carbon granulation (mm)	3–4	0.5–2.5

Application examples for impregnation of activated carbon with different chemicals [3]:

- Sulfuric acid: basic gas components, such as ammonia and amines, and mercury.
- Phosphoric acid: basic gas components such as ammonia and amines.
- Potassium carbonate: acidic gas components such as hydrogen chloride (HCl), hydrogen fluoride (HF), sulfur dioxide (SO₂), hydrogen sulfide (H₂S), nitrogen dioxide (NO₂) and carbon disulfide (CS₂).
- Potassium iodide: hydrogen sulfide (H₂S), phosphine (PH₃; also known as phosphane), mercury (Hg), arsine (AsH₃), radioactive gases and radioactive methyl iodide.
- Potassium permanganate: H₂S from oxygen-free gases, formaldehyde.
- Sulfur: mercury.
- Silver: drinking water filter (biocide), phosphine and arsine (AsH₃).
- Copper sulphate: odors and basic gas components.

Typical difficulties in estimating the dynamic loading are an unknown mass transfer zone, a mixture of substances with different adsorption behaviors, separation of the various substances during adsorption (chromatography), variable input concentrations and interfering substances such as lime and iron. Reference values for dynamic loading are summarized in Table 5. In process engineering, the throughput is the amount of substance flowing through a plant in a specific unit of time.

Table 5. Basic data for the design.

Type of Water	Loading (%)	Specific Throughput (m ³ /kg)	Bed Volume (L)
<i>Drinking water</i>			
Dissolved organic carbon (2 ppm; 99.99%)	ca. 6–10	30–50	10,000–20,000
Trace substances (10 µg/L; 95%)	0.03–0.19	30–200	11,000–70,000
<i>Industrial wastewater</i>			
Halogenated organic compounds (250 µg/L; 98%)	<1	<40	<16,000
<i>Landfill leachate</i>			
Chemical oxygen demand (1.000 ppm; 95%)	≤60	0.6	250

7.5. Drinking Water Treatment

Granular activated carbon filters have a traditional application in drinking water treatment plants. This form of activated carbon is (almost) always used at the end of a chain of processing steps to remove foreign substances and pollutants. In comparison, powdered activated carbon is commonly used at the head of water treatment plants. The use of biological activated carbon (no thermal reactivation) has gained popularity, but process control is a challenge [1,3].

7.6. Swimming Pool Water Treatment

The removal of free chlorine (HOCl) and trihalomethanes is an important goal in swimming pool water treatment. However, the use of reactivated activated carbon, previously used in a variety of industrial applications, should be avoided. (Metal-based) salts can remain on the activated carbon because of the reactivation. When used again in aqueous media, these can be released from the activated carbon and could possibly lead to irritation or damage to swimming pool users. In general, however, reactivated activated carbon, which was previously used in non-critical applications such as drinking water treatment, can also be used to treat swimming pool water. Coconut-based activated charcoal is also considered safe.

Contaminated activated carbon should therefore not be reactivated and reused for water treatment. Saline water with an electrical conductivity of >3000 µS/cm often contains ions such as calcium(II) ions (Ca²⁺), carbonate anions (CO₃^{2−}), sulphate anions (SO₄^{2−}) iron(III) ions (Fe³⁺), chloride anions (Cl[−]) and nitrate anions (NO₃[−]) in undesirably high concentrations.

High electrical conductivity is an indication of high salt (ionic) content. Ions are also in the pore system together with the water. In the first step of reactivation (drying), ions precipitate as salts and accumulate in the pores. Salts remain in the pores during the second reactivation step (combustion of the carbon at temperatures exceeding 800 °C). Some salts based on Ca²⁺ can act as fire accelerators. In addition, salt can also block pores. The ash content then increases significantly.

7.7. Car Wash Wastewater Treatment

Activated carbon is also used in industrial wastewater treatment [26]. This includes the cleaning of silo vehicles. Wastewater from car washes is collected and a portion is evaporated. Recovery would be technically possible.

The exhaust air from the evaporator is cleaned by adsorption. The distillate from the evaporator system enters the inclined separator. The overflow from the lamella separator is treated in an activated carbon stage. The lamella clarifier effectively separates settleable substances (particles) from liquids and is mainly used in the treatment of process water and wastewater.

A very high loading of the activated carbon with substances that increase the chemical oxygen demand is often necessary. However, the ratio between the biochemical oxygen demand and the chemical oxygen demand is mostly around one to two, which is an indication that organic components should be readily biodegradable by microorganisms [26].

Optimizations of the cleaning stage are, however, possible. The lamella clarifier could be designed better. An optional filtration stage (e.g., gravel filter) would also be helpful. A sequential biological purification process for biological treatment would also be conceivable to reduce the high biochemical oxygen load. An activated carbon filter stage could be possible to minimize the chemical oxygen demand load both in the effluent and in emergency operation.

7.8. Gas Phase: Errors in Adsorbers

A typical starting scenario when assessing challenges with activated carbon adsorbers in practice is an insufficient adsorber to retain solvents. The goal is often to get concentrations of ethyl acetate, methanol, ethanol or isopropanol below 50 mg/m^3 . Changing the mixtures of substances with variable concentrations are often detected.

The adsorber serves to retain certain solvents. Parameters such as flow, temperature, relative humidity, grain diameter and bulk height must be determined.

Common malfunctions are, for example, a partial spontaneous or early breakthrough of various substances, insufficient service life, desorption when changing loads and reduced working capacity. Typical sources of error are a relatively high temperature, a relative humidity that is slightly too high, a filter speed that is too low or too high, a non-optimal type of activated carbon and the presence of only one adsorber.

The adsorber process should be optimized. Two adsorbers could be connected in series. The first adsorber serves high loads. The second adsorber has the function of a police filter (reserve) in case the first filter breaks through. Different activated carbon types and recirculation lines should also be considered. An alternative to two adsorbers in series could be redundancy through two parallel lines.

Another possible solution would be to use three to four adsorbers connected in series. The adsorbers could be filled with different types of activated carbon. In general, adsorbers can be improved by the following measures: lowering the temperature, reducing the relative humidity, increasing the dimensions of the adsorber, increasing the volume flow, using types of activated carbon with larger pores and installing police filters.

7.9. Desulfurization of Natural Gas

Natural gas is a powerful energy source. However, it can only be optimally used if it is free of hydrogen sulfide. This highly toxic gas contaminates natural gas. If it is not bound with adsorbers, sulfur dioxide is produced during combustion. This is a gas that contributes massively to air pollution. Among other challenges, it causes acid rain (i.e., precipitation with pH values around 4.2–4.8), which harms people, animals and plants.

Water and sulfur severely corrode pipelines and processing plants. The tubes and pipes corrode (decompose) very quickly and would have to be replaced frequently if natural gas was not desulfurized first.

To make natural gas usable, it needs the desulfurization process. Producers usually carry these processes out directly during sourcing, i.e., even before the gas is transported to the consumer via pipelines and pumped into huge storage facilities. This is where the next challenge arises. Sulfur can also be produced in underground storage facilities: either from the rock or from natural processes of decomposition. Before the gas can be fed into the grid, it must be freed from hydrogen sulfide again.

Natural gas is passed through large adsorbers for desulfurization. These are often filled with activated carbon. Highly active charcoals allow for full loading. A ton of activated carbon can absorb a ton of sulfur. Theoretically, loads of more than 100% are also possible. Specially impregnated, it optimally meets high requirements.

The following is a list of important design parameters that must be compiled with the customer to optimize the desulfurization of natural gas: volume flow, temperature, oxygen concentration, pressure, relative gas humidity, inlet concentration, target concentration, inlet load components, activated carbon used, achievable loading, activated carbon requirement (e.g., per hour and in total) in terms of volume and mass, service life until adsorber exhaustion, adsorbed load, inner diameter of the container, bulk density of the activated carbon, filter speed, empty pipe residence time and pressure drop. The desulfurization process could be controlled, for example, by injecting oxygen (also air) and by increasing the moisture content.

7.10. Catalysts Based on Activated Carbon

Activated carbon can be used as a support for catalysts. In chemistry, catalysts based on activated carbon are used. The activated carbon serves as a carrier for transition metals such as palladium, platinum and rhodium. A typical area of application for these catalysts is catalytic hydrogenation.

In chemistry, hydrogenation is the addition of hydrogen to other chemical elements or compounds. A chemical reaction that is very frequently carried out in organic chemistry is the additive hydrogenation of carbon–carbon (C–C) double bonds.

The trigger for the development of activated carbon as a catalyst was the need for denitrification (i.e., the removal of various nitrogen oxides) and desulfurization of flue gases as simultaneous separation at low temperatures. Flue gas comprises a mixture of gases resulting from, for example, combustion in a furnace and passing off through the smoke flue.

Stricter regulations for air pollution control increased interest in catalysts that work at temperatures of around 120 °C and can therefore be installed downstream of the flue gas scrubber. This is economically advantageous. In comparison, selective catalytic reduction works at around 300 °C (see below).

The activated carbon affects catalytic activity. However, this activity is not proportional to the free surface areas of the micro- and submicropores. The catalytic activity takes place at the so-called active centers. Such centers arise at the edges of the graphitic structure by unsaturated carbon atoms ($\dots \text{C}=\text{C} \dots$) or by heteroatoms (N and O).

The active centers are determined by measuring the chemisorption of oxygen under defined conditions. The temperature plays a significant role in the formation of active centers during carbonization.

Special low-ash hard coal is used as the raw material for the production of activated carbon as a catalyst. An oxidative pre-treatment minimizes caking. The (partly) oxidized coal dust is mixed with water as a binder and extruded. In process engineering, extrusion is defined as forcing viscous materials through a die. The applications of activated carbon as a catalyst are diverse:

- Parallel retention of nitrogen oxides and sulfur dioxide;
- Glass melting furnaces;
- Cement manufacture;
- Waste incinerators;
- Plants for thermal soil remediation;
- Exhaust air from vehicle tunnels;
- Decomposition of hydrogen peroxide and ozone;
- Retention of Fe^{2+} and Mn^{2+} in water.

8. Other Carbonaceous Adsorbents

8.1. Activated Coke

8.1.1. Description and Application Areas

In addition to activated carbon, other carbon-containing adsorbents are also important. Section 8 briefly discusses activated coke [27], biochar [28] and carbon molecular sieves [29]. Readers are advised to refer to review articles [27–29] for more information.

Activated coke is a carbon-based adsorbent that is usually obtained from lignite, bituminous or hard coal. It is mainly used to clean exhaust gases. Due to its pore distribution, activated coke is suitable for separating polychlorinated dibenzodioxins and dibenzofurans. Activated coke is commonly used when regeneration of the adsorbent is not particularly easy. This coke is often further processed with hydrated lime to form mixed sorbents [9].

Activated coke is obtained through the pyrolysis of lignite or (hard) coal with subsequent thermal activation. Compared with activated carbon, activated coke has a smaller specific surface area and a different pore size distribution. The volume of micropores is smaller in coke. Activated coke has two frequency peaks at meso- and macropores.

8.1.2. Carbon-Based Selective Catalytic Reduction

Carbon-based selective catalytic reduction is a dry exhaust gas cleaning process for reducing pollutants in exhaust gases from industrial plants such as waste incinerators, steel mills and coal-fired power plants. The process is characterized by a single- or multi-stage activated coke (Section 8.1.1) moving bed reactor that is operated in counter current.

In the carbon-based selective catalytic reduction process, activated coke serves both as a catalyst for the oxidation of certain exhaust gas components and as a storage medium for adsorbed sulfur dioxide in the form of sulfuric acid or other pollutants. The loaded activated coke is discharged and can be regenerated.

For denitrification, a nitrogen-oxide-reducing gas, usually ammonia, is added to the exhaust gas after sulfur dioxide has been separated out. Nitrogen oxide is then converted into nitrogen and water together with ammonia in another bed of activated coke in the presence of activated coke as a catalyst. In addition to nitrogen and sulfur oxides, other pollutants such as dioxins and furans, dust, heavy metals such as mercury and halogens such as hydrogen fluoride and hydrogen chloride are also separated due to the diverse properties of activated coke.

The carbon-based selective catalytic reduction technology is an adsorptive and absorptive dry moving bed process. The flue gas (Section 7.10) is routed in the opposite direction to the flow of adsorbent using the countercurrent principle. The flue gas is conducted at a temperature of 90 °C to 140 °C into the flue gas collection space below the activated coke bed. From there, the gas enters an activated coke bed. If necessary, a second activated coke bed is installed downstream of the first.

The first bed is usually used to separate sulfur oxides and dust. The dust contained in the exhaust gas is separated due to the filter effect of the activated coke bed. Sulfur dioxide contained in the exhaust gas is catalytically oxidized to sulfur trioxide on the surface of the activated coke and reacts with water vapor to form sulfuric acid, which is chemically absorbed in the pore system of the activated coke. In addition to sulfur dioxide and dust, other pollutants are also adsorbed by the activated coke.

Denitrification takes place in the second bed. Before the flue gas enters the second bed, it is fed into a mixing chamber to which gaseous ammonia water is added. The nitrogen oxides in the flue gas react with the added ammonia on the catalytic surface of the activated carbon to form the harmless products nitrogen and water. The flue gas leaves the second bed and can be discharged cleaned into the ambient air via a chimney.

The structural design of the adsorber inflow floor ensures, on the one hand, an even distribution of the flue gas when it enters the activated coke bed and, on the other hand, ensures that the bed sinks in a plane-parallel manner when the loaded activated coke is discharged.

When the discharge device is actuated, the activated coke enters the discharge funnel. The activated coke bed is lowered by a few millimeters. As a result, fresh activated coke automatically slides out of the storage bunker into the adsorption area of the adsorber.

The countercurrent principle ensures that the activated carbon is loaded evenly over the entire inflow area. Better activated coke loading also takes place. This leads to the minimization of activated coke consumption. Only the most highly loaded layer of activated

carbon is drawn off in almost any adjustable batch via the simple and regulated draw-off. Activated coke can be regenerated with thermal treatment.

8.2. Biochar

Biochar is the light and black residue of carbon and ash that remains after the pyrolysis of biomass [28]. This is a form of charcoal. Biochar is the solid material obtained from the thermochemical conversion of biomass in an oxygen-poor environment. This sustainable material can remain in the soil for thousands of years.

Biochar can sequester carbon with minimal effort and is a means of mitigating climate change. Biochar can increase the soil fertility of acidic soils and increase agricultural productivity. Biochar is primarily used for soil application and is known to improve soil nutrient availability, soil aeration and soil water filtration [9].

Biochar is an environmentally friendly soil material. However, potential negative effects of biochar have to be considered, e.g., the disruption of the pH of a soil or the introduction of harmful chemicals that cause problems at the microlevel [9].

8.3. Carbon Molecular Sieve

A molecular sieve is a natural or synthetic zeolite or another substance that has a high adsorption capacity for gases, vapors and dissolved substances with certain molecular sizes. With a suitable choice of molecular sieve, it is possible to separate molecules of different sizes [29].

In addition to zeolites, there are also carbon molecular sieves (CMS). Depending on the process, these are often somewhat more expensive but can be specialized for a specific separation during pyrolysis.

Application examples are diverse. To obtain high-purity nitrogen, for example, manufacturers often rely on pressure swing adsorption. Compressed air is fed alternately into two containers. These are filled with a carbon molecular sieve. This is how oxygen molecules are trapped. High-purity nitrogen remains. It is routed to downstream collection tanks. From there it can be fed directly into the customer's network.

9. Conclusions and Second Part of the Special Issue

This teaching handbook has outlined adsorption processes, characterized the mechanical, chemical and adsorption properties of activated carbon, outlined important application technologies and also introduced other carbonaceous adsorbents. It is an academic but applied reference guide for practitioners new to the subject area of adsorption with carbonaceous products.

This handbook-style tutorial introduces the first part of the special issue on Recent Advances in Applied Activated Carbon Research. The second part of this issue is concerned with technical and full research papers focusing on advanced topics such as complex activated carbon application technology, sustainable biochar applications, biological regeneration of activated carbon, novel bioreactors, carbon-based materials, carbon molecular sieve membranes, carbon-based chemical engineering and clean technology applications, the design of adsorbers, multi-stage fluidized bed reactors, novel technologies to remove PFAS and thermal reactivation of activated carbon.

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