

Chapter 2

Historical Production and Use of Carbon Materials: The Activated Carbon

2.1 Introduction (Activated Carbon)

The use of carbon extends far back to 3750 BC, for the reduction of copper (Cu), zinc (Zn), and tin (Sn) ores in the manufacture of bronze by the Egyptians and Sumerians. In 157 AD, carbons of both vegetable and animal origin had been used for the treatment of a wide range of diseases. In the year 1773, Car Wilhelm, a chemist from Pomerania, a Baltic coast of Europe under Swedish control, recognized the absorptive power of carbon-derived materials from different sources. However, marketing of first industrially produced *activated carbon*, *Eponit* (trade name), was first reported in the year 1911 by the Fanto Works, Austria [1]. The largest market for activated carbon is currently in the municipal water purification industry.

Activated carbon, also called *activated charcoal*, *activated coal*, or *carbo activatus*, is a microporous *inert carbon* with large internal surface area in excess of $500 \text{ m}^2/\text{g}$, which has been measured from absorption isotherms of carbon dioxide (CO_2) gas at room temperature (300 K) [2–3]. Activated carbons (ACs) are complex products which are difficult to classify on the basis of their behavior, surface characteristics, and other fundamental criteria. However, some broad classification is made for general purpose, based on their size, preparation methods, and industrial applications: powdered activated carbon (RI, PAC), granular AC (GAC), extruded AC (EAC), bead AC (BAC), impregnated AC, and polymer-coated AC.

Riddled with small, low-volume pores, the large internal surface area has been a fascinating quality of the magnificent elements that have revolutionized in material science and modern industry for their unique absorbing power. Since *activated carbon* (AC) has high degree of microporosity, 1 gram of AC can give a surface area between 600 and 1200 square feet.

2.1.1 Activated Carbon (AC)

Activated carbon when viewed under electron microscope shows high surface area structures as shown in Fig. 2.1. Individual particles are intensely convoluted and show various kinds of porosity. In some areas, one can notice graphite-like flat surfaces that run parallel to each other separated by a few nanometers or so. The micropores of activated carbon (AC) provide excellent conditions for absorption to occur, since the absorbing material can interact with many surfaces simultaneously [4].

Activated carbon (AC) is one of the most important microporous adsorbents due to its tremendous adsorptive capacity, an affinity for a variety of dissolved organics, and ability to be custom-tailored to suit specific applications [5]. Figure 2.2 shows some pores and their structures in AC.

It is used in gas purification, decaffeination, gold purification, metal extraction, water purification (Fig. 2.3), medicine (Fig. 2.4), sewage treatment, air filters in gas masks and respirators, filters in compressed air, and many other applications. It was James Dewar, a scientist, who first invented Dewar (vacuum flask, one of the essential commodities) and studied AC in detail, especially its absorption capacity [6].

Figure 2.2a represents the hypothetical pores of activated carbon used in water filtering system, and Fig. 2.2b represents pores of activated carbon seen under

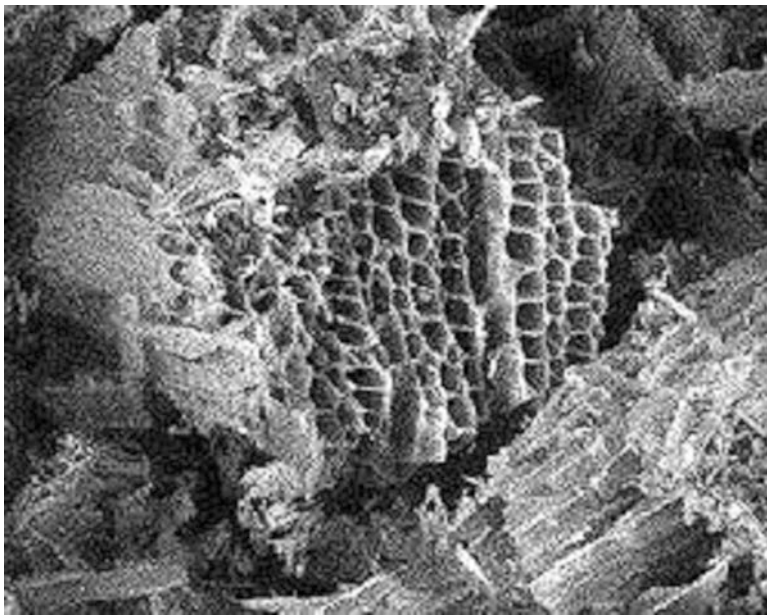


Fig. 2.1 shows a micrograph of activated carbon under an electron microscope (Photo courtesy: WIKI)

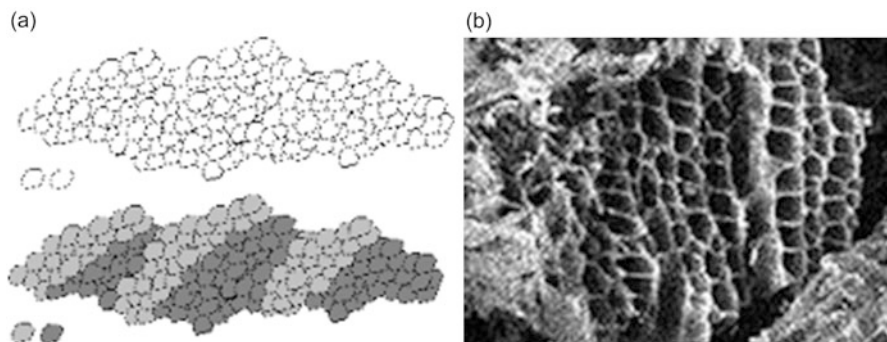


Fig. 2.2 (a) Representation of the hypothetical pores of the activated carbon used in water filtering system; (b) Pores of activated carbon seen under electron microscope (Courtesy: WIKI)

electron microscope. Granular activated carbon (GAC) has relatively larger particle size compared to powdered activated carbon, and consequently presents a smaller external surface. These carbons are therefore used for adsorption of all gases and vapors as their rate of diffusion is faster. GAC is designated by sizes such as 8×20 , 20×40 , or 8×30 for liquid phase applications and 4×6 , 4×8 , or 4×10 for vapor phase applications. A GAC-designated size 20×40 means that the filter is made of carbon particles that would pass through a U.S. standard mesh size No. 20 sieve (0.84 mm) but be retained on a U.S. standard mesh size No. 40 sieve (0.42 mm). The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation, and it is the spaces between the crystals which form the micropores. The pore diameter of a typical activated carbon can vary from $<20 \text{ \AA}$ to $>5000 \text{ \AA}$. Porous carbons can contain several impregnated inorganic elements such as iodine (I_2), silver, cations such as aluminum (Al), manganese (Mn), zinc (Zn), lithium (Li), and calcium (Ca) for specific applications [7–8].

Activated carbon (AC) has been used in water filtration system using polyvinyl chloride (PVC) pipe. Figure 2.3 shows the use of AC in water filtration system which consists of pebble, palm, palm fiber, alum, activated carbon (AC), gravel, chlorine (Cl_2), smooth sand, and gravel (from bottom to top). Each ingredient is separated with sponge filtration and gauge to keep it at fixed place.

Activated carbon (AC) is used to treat poisonings and overdoses following oral ingestion. Figure 2.4 shows a commercial product where activated carbon is being used for medical use.

Activated carbon can be considered as a material of phenomenal surface made up of millions of pores comparable to a molecular sponge. The process in which such a surface concentrates fluid molecules by chemical or physical forces through the pores is known as *adsorption* – the adhesion of the ions, atoms, or molecules from a gas or a liquid or dissolved solid to a surface [9–10]. The word adsorption was coined in 1881 by German physicist Heinrich Kayser [10–11]. Adsorption is generally described through isotherms, that is, the amount of adsorbate on the

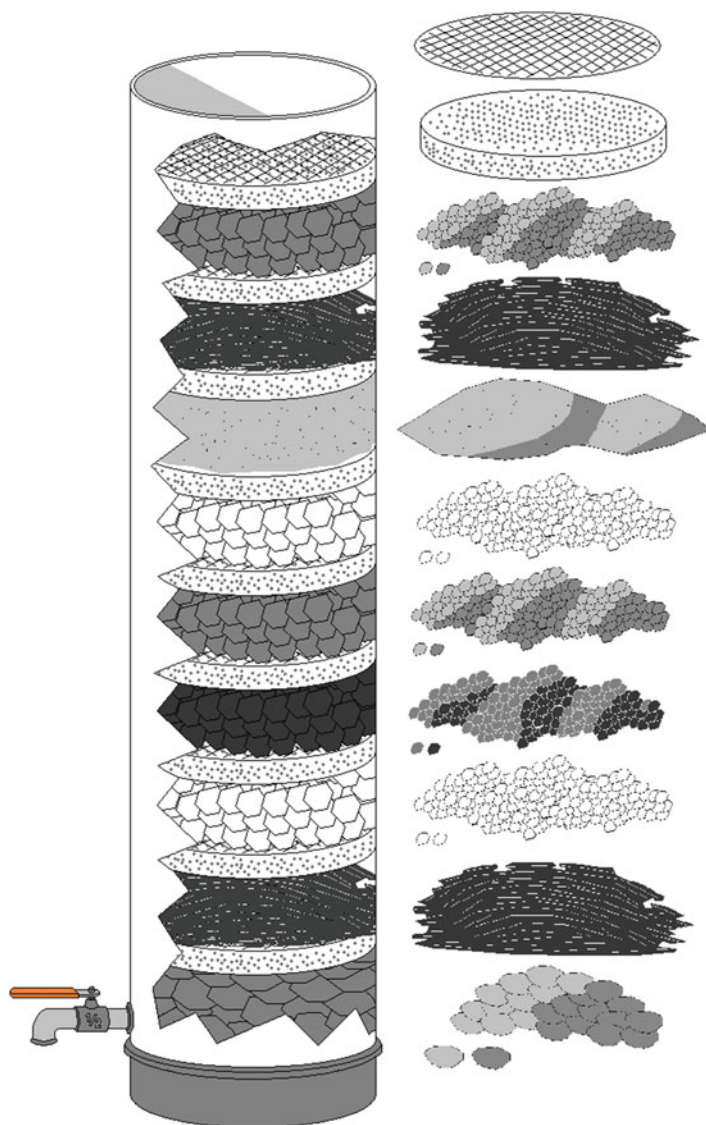


Fig. 2.3 Water filtering system with activated carbon and other ingredients (Courtesy: Iran Akira, WIKI)

adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of adsorbent to allow comparison of different materials. To date, there are more than 15 models that have been put forward by different investigating scientists. We will discuss some of the models.

Fig. 2.4 Activated carbon
being used in medicine
(Photo courtesy:
S. Heilman, WIKI)

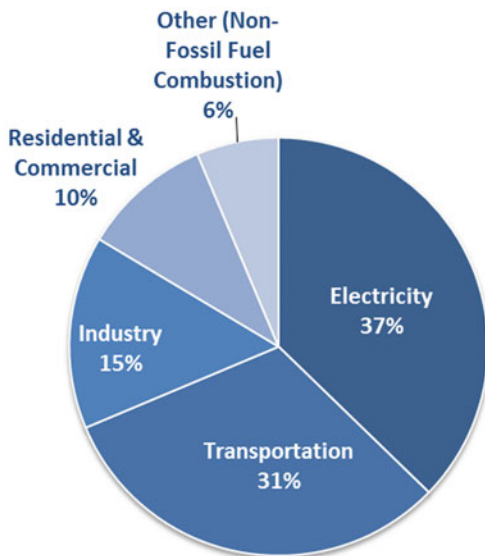


Physically, AC binds materials by van der Waals or London dispersion force. But they are unable to bind certain chemicals like alcohols, glycol, strong acids and bases, metals and most inorganics like lithium (Li), sodium (Na), iron (Fe), lead (Pb), and arsenic (As). Similar problems arise with carbon monoxide (CO).

Carbon dioxide (CO₂) emission from carbon-emitting fuels such as coal, petroleum, and natural gas causes lots of dreadful impacts on the ecology. Global warming is also believed to be due to the large emission of CO₂ gas in the atmosphere (Fig. 2.5) [12].

Global Warming Potential (GWP) was developed to allow comparisons of the global warming impacts of different gases. Specifically, it is a measure of how much energy the emissions of 1 ton of a gas will absorb over a given period of time, relative to the emissions of 1 ton of carbon dioxide. The larger the GWP, the more that a given gas warms the Earth compared to carbon dioxide over that time period. The time period usually used for GWPs is 100 years. GWPs provide a common unit of measure, which allows analysts to add up emission estimates of different gases (e.g., to compile a national greenhouse gas inventory), and allows policymakers to compare emission reduction opportunities across sectors and gases. Carbon dioxide (CO₂), by definition, has a GWP of 1 regardless of the time period used, because it is the gas being used as the reference. Carbon dioxide remains in the climate system for a very long time: carbon dioxide emissions cause increases in atmospheric concentrations of carbon dioxide that will last thousands of years [13].

Fig. 2.5 shows US CO₂ emission (inventory of US greenhouse gas emission sinks (1990–2013) (Source: EPA, USA, Ref. 13)



Mercury, a highly toxic trace element, is of particular concern because, during coal combustion and municipal waste incineration, most of the mercury present in the fuel is transferred into vapor phase, due to its high volatility. In postcombustion environment of a boiler, it is transformed to oxidized forms (Hg^{2+} X_g). Most of the existing air pollution control technologies, such as electrostatic precipitators and baghouses, cannot remove effectively gas phase mercury emission, except for particle-bound atoms (Hg_p) [14].

Activated carbon materials are believed to be the most attractive absorbant for CO₂ gas and vapor phase mercury (Hg), due to its low cost, low sensitivity to moisture, and high stability.

Isotherm equations that deal with physical adsorption of gases and vapors give the most important characteristics of industrial sorbents that include, among others, pore volume, pore size or energy distribution, and specific surface area. The correct interpretation of experimental adsorption isotherms can be realized in terms of mathematical adsorption equations [15].

In 1914–1918, Langmuir proposed a mathematical equation for the adsorption mechanism as



where A is a gas molecule and S is an absorption site. If we define surface coverage, θ , as the fraction of the absorption sites occupied in the equilibrium condition, we can write

$$K = (\theta)/(1 - \theta) P \quad (2.2)$$

$$\text{Or } \theta = (KP)/(1 + KP), \quad (2.3)$$

where P is the partial pressure of the gas or molar concentration of the solution. For very low pressure, the value of $\theta \approx KP$, and for high pressure, the value of $\theta \approx 1$. Experimentally, the parameter θ is difficult to measure. To ease the mathematical calculations, the parameter θ has been replaced by the ratios of the gas volume, as $\theta = (v/v_{\text{mon}})$, where v_{mon} is the gas volume occupied at standard temperature and pressure (STP). Replacing the value of θ in Eq. (2.3), we can write Eq. (2.3) as

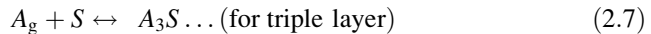
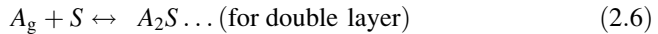
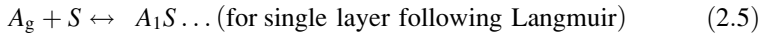
$$(1/v) = (1/(K v_{\text{mon}})) (1/P) + (1/v_{\text{mon}}) \quad (2.4)$$

The slope of the curve and the y-intercept will give the values of v_{mon} and K , which are constant for each adsorbent/adsorbate pair at a given temperature. It is noteworthy that the Langmuir studies of gas adsorption led to the formulation of a general treatment of kinetics of reactions at the surfaces, and in 1932, he was awarded the Nobel Prize in Chemistry for his discoveries and researches in the realm of surface chemistry [16].

2.1.2 Adsorption–Desorption

Often, molecules do form multilayers because some of the molecules are adsorbed on already adsorbed molecules. Langmuir isotherm formulation was inadequate to solve the problem for multilayers. However, in 1939, Stephen Brunauer, Paul Emmett, and Edward Teller (BET) developed a model isotherm which can be extended to the finite n number of adsorbed layers [17–19].

Figure 2.6 shows the schematic of the BET model of multilayer adsorption. The distribution of the particles on the material surface is random. The BET theory, despite many restrictions, was the first attempt to create a universal theory of physical adsorption [20]. The theory goes by the three names and hence called BET theory, the modified Langmuir's mechanism, and it follows as



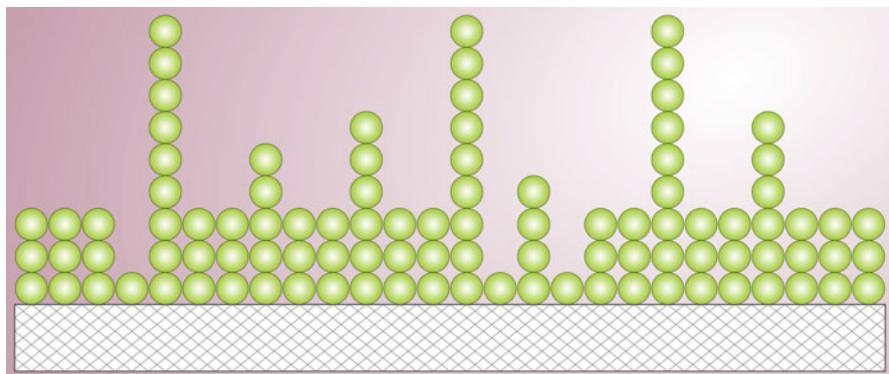


Fig. 2.6 Schematic of the BET model of multilayer adsorption (Courtesy: Riely, Creative Comm., WIKI)

The derivation of the formula is much more complicated than Langmuir's single layer model, and for multiple layers we can write the equation as

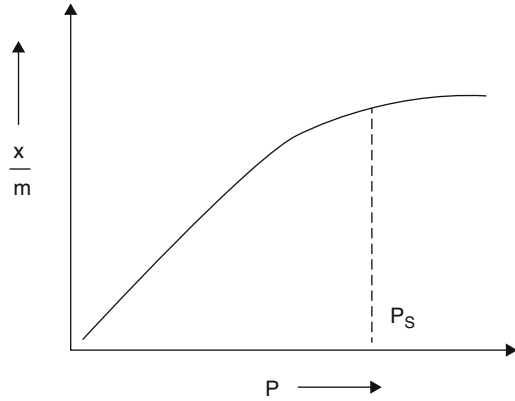
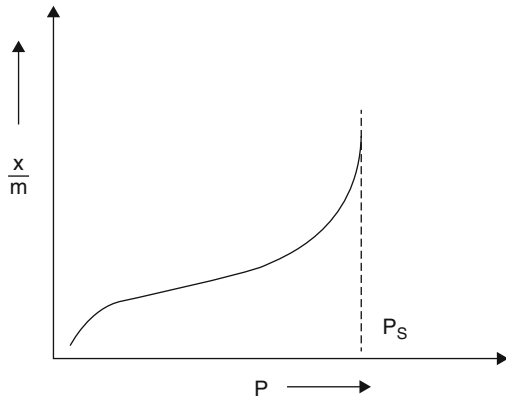
$$\{p/(v(1-p))\} = 1/v_{\text{mon}}c + \{p(c-1)\}/\{v_{\text{mon}}c\} \quad (2.9)$$

where $p = (P/P_0)$ is pressure divided by the vapor pressure for the adsorbate at that temperature, v is the STP volume of the adsorbed adsorbate, v_{mon} is the STP volume of the amount of adsorbate required to form a monolayer, and c is the equilibrium constant ($K \times$ the vapor pressure of the adsorbate). The Langmuir isotherm is usually better for chemisorption, and BET isotherm works better for physisorption.

The BET theory has been further modified by Dublin and Radushkevich (DB) [21], and later by Polanyi [22]. According to their concept, multilayer adsorbed layer is not a two-dimensional problem as followed by Langmuir theory, but it possesses a definite volume and applies Van der Waals equation. Polanyi assumed that the adsorption potential is independent of temperature over a wide range. Such a statement follows from the fact that the van der Waals forces are also independent of temperature, which does not hold always for polar adsorbates.

Considering different two-dimensional (2D) adsorptional isotherms, different theories have been put forward from time to time. Some of these theories are worth mentioning, e.g., the Henry law for ideal non-localized monolayer, the Langmuir equation for ideal localized monolayer [23], the Volmer and the Hill-de-Boer [24] equations for the nonideal and nonlocalized monolayers, and the Fowler-Guggenheim [25] equations for the nonideal. However, among all of these theories the localized monolayers are worth mentioning. The 2D equations of state are very useful for investigating the phase transitions in the adsorbed layer [26–27].

The graph in Fig. 2.7 depicts monolayer adsorption (or type I adsorption isotherm), where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P [28–29]. The ratio of (x/m) is plotted against pressure (P). P denotes the saturation pressure. Type I adsorption isotherm is the adsorption of nitrogen (N_2) and hydrogen (H_2) on charcoal at temperature near to 1800 °C. In BET Eq. (2.9), if

Fig. 2.7 Type I adsorption isotherm**Fig. 2.8** Type II adsorption isotherm

the values of $(p) \ll 1$ and $c \gg 1$, then it leads to monolayer formation of type I (Fig. 2.7).

In type II adsorption isotherm (Fig. 2.8), we can see a large deviation from the Langmuir model of adsorption. The intermediate flat region is the isotherm that corresponds to monolayer formation. Examples of type II adsorption isotherms are N_2 gas adsorption at 1950 °C on iron (Fe) catalyst and N_2 adsorbed at 1950 °C on silica gel. Here, the value of c in Eq. (2.9) is very large.

Type III adsorption isotherm (Fig. 2.9) also deviates largely from the Langmuir model. If $c \ll \ll 1$ in BET equation, we can expect an adsorption isotherm similar to type III. In this curve, there is no flat portion which indicates that there is no formation of monolayer. Examples of type III adsorption isotherms are bromine (Br_2) or iodine (I_2) adsorbed at 790 °C on silica gel.

At low-pressure regions, type IV adsorption isotherm (Fig. 2.10) shows similarities with type II adsorption isotherm, indicating that at low pressure it forms monolayer and multilayers of adsorption. The saturation level is reached at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at

Fig. 2.9 Type III adsorption isotherm

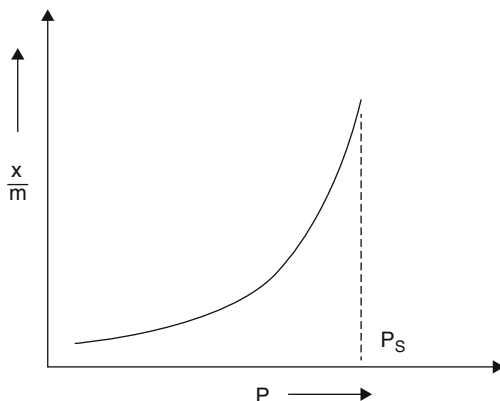
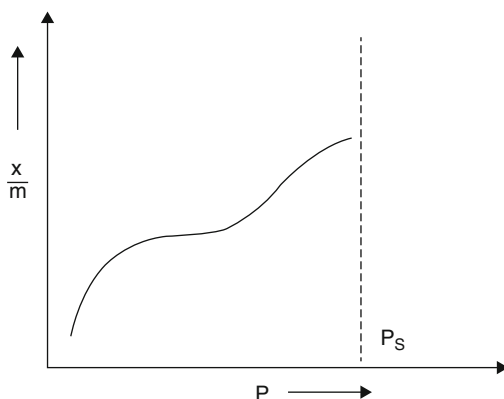


Fig. 2.10 Type IV adsorption isotherm



a pressure below the saturation pressure of the gas. Examples of type IV adsorption isotherm are of adsorption of benzene on iron oxide (Fe_2O_3) and on silica gel at 590°C .

The graph for type V adsorption isotherm (Fig. 2.11) is similar to type IV. Example of type V adsorption isotherm is adsorption of water on charcoal at 1000°C . The understanding of the adsorption isotherms is important in the solution of a large class of industrial problems on efficient and safe storage, and handling of gases during transportation. It has been proposed that flammable gases could be adsorbed on to a variety of adsorbents and transported and then released safely after their arrival [30].

In the case of adsorption where capillary condensation occurs, hysteresis loops appear [31–32]. Very recently, these hysteresis loops have been classified in a way similar to the International Union of Pure and Applied Chemistry (IUPAC) adsorption isotherm scheme (Fig. 2.12) [33].

The major progress made in the understanding of the adsorption, pore condensation, and hysteresis behavior of the fluids in the nanoporous materials has led to

Fig. 2.11 Type V adsorption isotherm

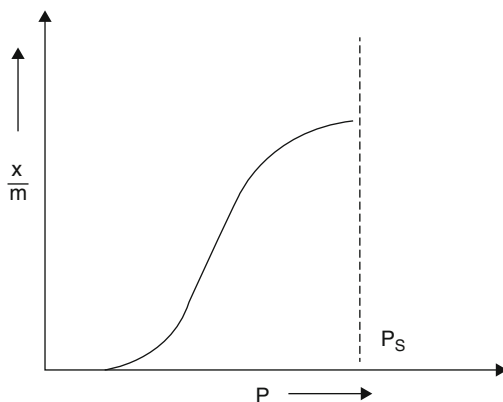
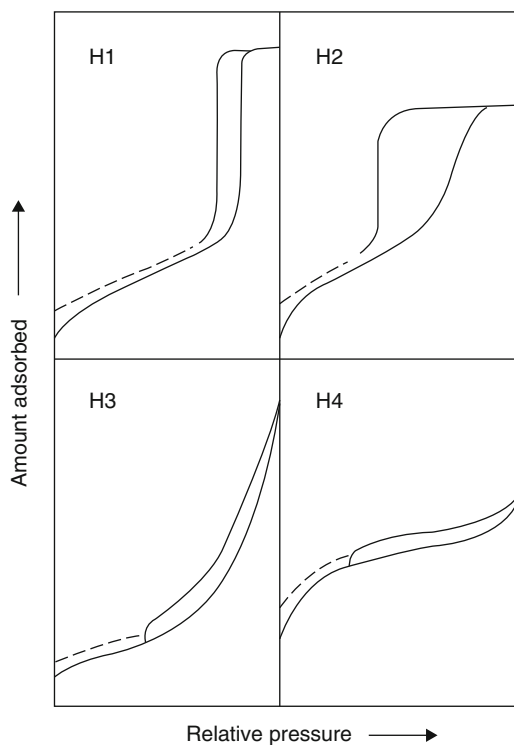


Fig. 2.12 Four IUPAC classifications of adsorption isotherms: Hysteresis loops



the development in the structural characterization by physical adsorption. The development and availability of advanced theoretical models on statistical mechanics like nonlocal density functional theory (NLDF) and molecular simulation also had helped in this endeavor. In spite of the progress made on the theoretical models

and computer simulation works, there still exist major problems in the characterization of disordered porous materials, especially mesoporous with inhomogeneous surface chemistry.

2.1.3 Kinetic Theory of Adsorption

According to some experimental observers the kinetic theory of adsorption in activated carbon, Fick's interparticle diffusion equation has been accepted as a more accurate model compared to linear driving force model for solving the desorption kinetics of CO₂ and Hg gases. Rates of adsorption and desorption in porous adsorbents are generally controlled by transport within the pore network, rather than by the intrinsic kinetics of sorption at the surface. It is convenient to consider interparticle transport as a diffusive process and to correlate kinetic data in terms of diffusivity defined by Fick's first law as [34–35]:

$$J = -D_{\text{eff}}(dC/dr) \quad (2.10)$$

where J is the diffusion flux, D_{eff} is the diffusivity {(length)²/time}, C is the concentration of the substance (amount of substance per unit volume (mol/m³)), and r is the radius of the porous catalyst (assuming to be spherical). We will focus our attention on the spherical shell of porous material contained within the region r and $(r + \delta r)$.

Now, {rate of input by diffusion at $(r + \delta r)$ } = rate of efflux by diffusion at r + lost amount due to chemical reaction, assuming that the stoichiometric coefficient of reactant is (-1)

and that there is no change in the number of moles on reaction. The balanced equations in mathematical form can be presented by

$$\left[4\pi r^2(D_{\text{eff}}(dC/dr))\right]_{(r+\delta r)} = \left[4\pi r^2 D_{\text{eff}}(dC/dr)\right]_r + K \rho S_g (4\pi r^2 \delta r) C \quad (2.11)$$

where K is the absorption rate constant, ρ is the apparent density of the catalyst particle (mg/cm³), and S_g is surface area per mg of the absorbent (cm²/mg). The differential equation governing simultaneous chemical reaction and diffusion becomes

$$(d/dr) (r^2 D_{\text{eff}} dC/dr) - K \rho S_g r^2 C = 0 \quad (2.12)$$

If the effective diffusivity is assumed to be constant, Eq. (2.12) will transform to

$$(d^2 C/dr^2) + \{(2/r) (dC/dr)\} - \{(K \rho S_g C)/D_{\text{eff}}\} = 0 \quad (2.13)$$

The above equation can be represented by Thiele modulus h_T (which is equal to {(diffusion time)/(reaction time)} [36–37] as

$$(d^2C/dr^2) + \{(2/r) (dC/dr)\} = (h_T/R)^2 C \quad (2.14)$$

where $h_T = R\{(K \rho S_g C)/(D_{\text{eff}})\}^{1/2}$. Now, we can solve this linear differential equation by introducing a new variable k_1 , where $k_1 = Cr$. Substituting this to Eq. (2.14) gives us

$$(d^2k_1/dr^2) = (h_T/R)^2 k_1 \quad (2.15)$$

The solution of Eq. (2.15) can be expressed in exponential form as

$$k_1 = Cr = C_1 e^{(h_T r/R)} + C_2 e^{-(h_T r/R)} \quad (2.16)$$

On the basis of pseudo-first order equation of Lagergren, kinetics of sorption on solid surfaces for liquid–solid phase sorption has been attempted by many investigators [38–41]. The linearized Lagergren pseudo-first order is generally expressed mathematically as

$$\log (q_e - q_t) = \log (q_e) - (k_1/2.303) t \quad (2.17)$$

where q_t and q_e are the sorption capacity at time t and at equilibrium, respectively (mg/g), and k_1 is the rate constant. Due to the presence of several variables, like agitation speed, sorbent diameter, solute concentration, sorbent mass, and solute temperature, the data with activated carbon following the pseudo-first order rate mechanisms show accuracy between 73% and 98%. In spite of many improvements in Langmuir, BET, and Lagergren theories, distinct deviation exists between the theory and the experimental observations. According to some critics, this might be due to heterogeneity of the most real solid sorbents [42].

Going back to 3759 BC, active carbon was first widely used as absorbent in the form of carbonized wood (charcoal). Porous solids are rapidly growing group of inorganic and organic compounds, and the most representative porous solids are activated carbon [43–47]. Discovery of molecular carbon structures as fullerenes, heterofullerenes, and carbon nanotubes (CNTs) has boosted the search for new selective adsorption applications of such materials.

2.1.4 Carbon Molecular Sieves (CMS)

Astonishing developments took place in the field of carbon-based materials such as carbon molecular sieve (CMS) and microporous and mesoporous carbons: MAXSORB (superhigh surface area microporous carbon, Kasai Coke and Chemicals Company, Japan) type material that has reached the theoretically possible limit of specific surface area, approaching 4000 m²/g. The *carbon molecular*

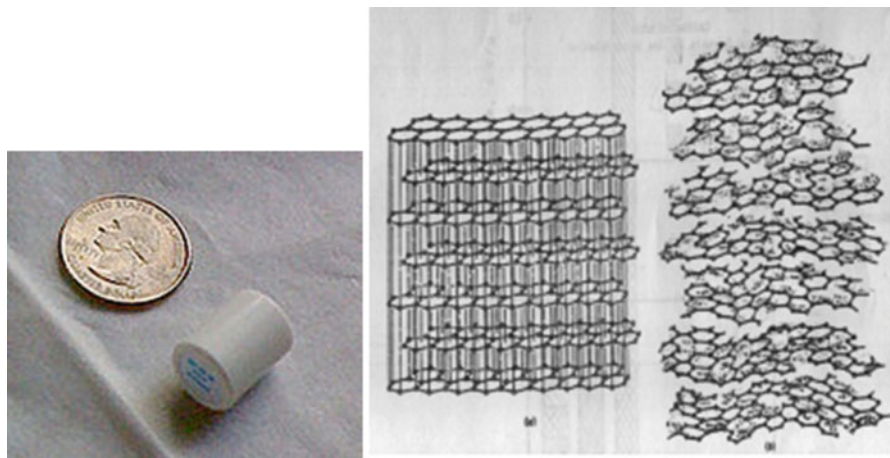


Fig. 2.13 A typical carbon molecular sieve, with pore size (3 Å–5 Å) (Courtesy: WIKI)

sieves (CMS) (Fig. 2.13), which are a special kind of activated carbon (AC) can discriminate moles on the basis of their shape and size. The main difference between these two carbonaceous structures may refer to their *adsorption kinetics*. The essential feature of AC is separation of molecules on the basis of differences in the adsorption equilibrium constant, whereas CMS separate molecules through differences in the adsorption rate of molecules [48]. As a matter of fact, CMS possess smaller pore size than AC; as a result, they are suitable for separation and purification of gas mixtures, e.g., nitrogen and oxygen from air; hydrogen and nitrogen from ammonia [49–50].

The production of CMS from lignocellulosic biomass involves three steps: pyrolysis of the starting material, activation of the prepared char, and modification of the pores of the activated carbon. Chemical vapor deposition (CVD) is typically applied to deposit carbon at the pore mouth to narrow down (modify) the size of the pores. Benzene, methyl pentane, and methane have been used as carbon sources to deposit carbon at the pore mouth [51–52].

The preparation for activated carbons (ACs) generally is performed by following two steps: (a) carbonization and (b) carbon activation. There are two methods that are followed to produce activated carbon. The first method is called physical reactivation, where the carbonaceous material is thermally decomposed in the range 600–900 °C in the absence of oxygen (inert atmosphere, like nitrogen or argon), and the noncarbon species are eliminated during the operation. The carbon mass thus obtained consists of closed pores or micropores that are activated in an oxidizing atmosphere, e.g., in the presence of oxygen, carbon dioxide, or steam, to enlarge the diameter of the small pores [53].

In chemical activation process, the carbonaceous material is treated with either phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), nitric acid (HNO_3), or with strong

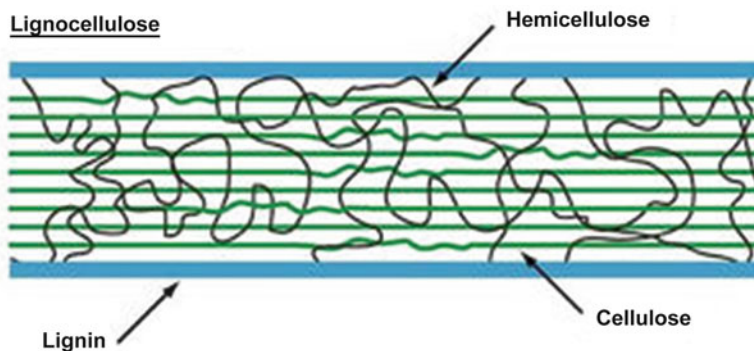


Fig. 2.14 Structure of lignocellulose (Courtesy: Shahrzad.khayat, Microbe WIKI)

bases like sodium hydroxide (NaOH) or potassium hydroxide (KOH), and then carbonization process is performed at lower temperatures (450–700 °C) [54–55].

The concentration of acid in chemical activation process is approximately 50% (w/w), and the activation temperature varies between 350 and 600 °C. Phosphoric acid with the maximum impregnation ratio has been found to produce the largest S_{BET} (BET stands for Brunauer-Emmett-Teller theory, which aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of surface area, S_{BET} , $\sim 1785\text{--}1802\text{ m}^2\text{ g}^{-1}$). However, with KOH and NaOH, one can obtain higher specific surface areas ($>100\text{ m}^2\text{ g}^{-1}$), but as these two chemicals (KOH and NaOH) are very corrosive, utmost care should be taken during operations [56].

The carbonaceous materials are of lignocellulosic origin. Lignocellulosic materials consist of cellulose, hemicellulose, and lignin (Fig. 2.14), and are the family of wood and wood products (Fig. 2.14). These materials are natural, abundant, and renewable resources essential to the functioning of the industrial societies and critical to the development of a sustainable global economy [57]. All types of cellulose microfibrils are composed of linearly linked β -(1 $\rightarrow$ 4) D glucopyranose units and differ only by the degree of polymerization. The remaining polysaccharides are known collectively as hemicellulose.

Lignocellulosic biomass (LB) is a potential inexpensive source of fuel which can replace the more expensive biohazard petroleum. All the chemicals derived from it (LB) will have a lower environmental impact than petrochemicals. Additionally, it is considered carbon dioxide-neutral, because burning it with coal in power plant does not add carbon to the environment beyond what is required for the process of growth. The future of extracting chemicals from lignocellulosic biomass appears to be bright, and it is hoped that use of this biopotential material will reduce US dependence on fossil fuels and ultimately develop a renewable resource based economy [58].

Figure 2.15 shows the molecular structure of lignin, cellulose, and hemicellulose. Lignin is a complex polymer of aromatic alcohols, having high molecular weight (HMW) and formulated by enzyme-initiated free radical polymerization of

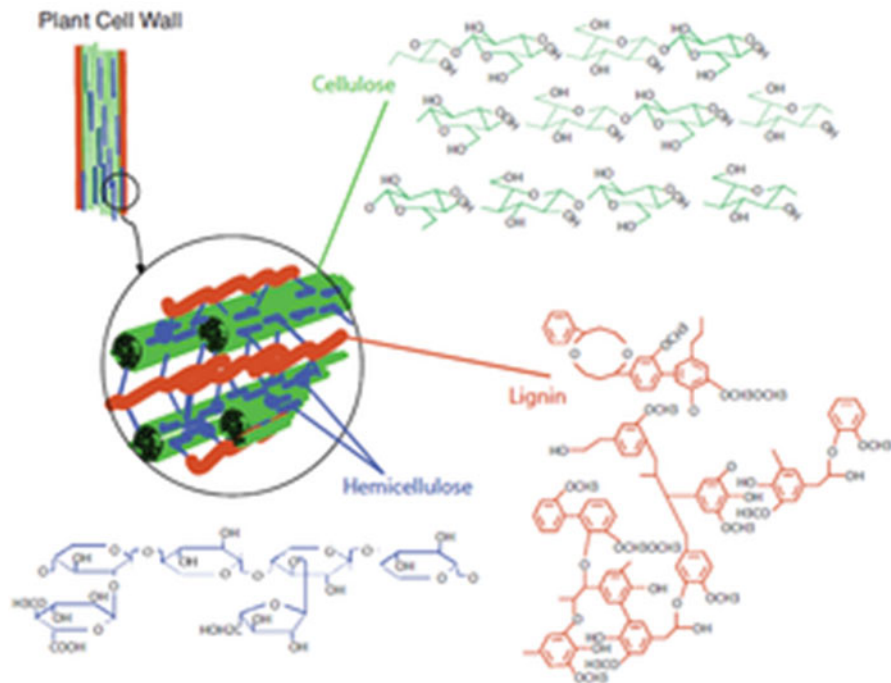


Fig. 2.15 Molecular structure of lignin, cellulose, and hemicellulose (Courtesy; WIKI)

coniferyl alcohol plus sinapyl alcohols. Lignin acts as a binding agent for the cellulose and hemicellulose fibers through a variety of linkages involving either carbon–carbon bonds of aromatic rings or propyl side chains [59–60].

2.1.5 Applications of Activated Carbon

Activated carbons and their products are very complex and hard to differentiate on the basis of their behavior, surface characterization, and preparation methods. However, some classifications have been made on the basis of their physical characteristics.

The first one chosen here is powdered activated carbon (PAC), having fine granules of diameter less than 1 mm in size, with an average diameter, surface to volume ratio, and a small diffusion distance. These ACs are used in raw water intakes, rapid mix basins, clarifiers, and gravity filters. The next one is called granular activated carbon (GAC). It has larger particles than the powdered AC. Because of larger diameters, they are preferably used for absorption of all gases, deodorization, and in rapid mix basins.

The third one is a powered AC mixed with a binder and shaped into a cylinder to be used for gas phase applications, and they are named as extruded AC or EAC. The diameter of the cylinder varies from 0.8 to 130 mm. The cylinders have high mechanical strength and contain very less dust particles. Similar to EAC, there is another AC family member, named as bead ACs or BAC. They are very similar to EAC in mechanical strength and dust content. For its spherical shape, it is preferred for fluidized bed applications.

Several inorganic chemicals such as iodine (I), silver (Ag), aluminum (Al), manganese (Mn), zinc (Zn), iron (Fe), lithium (Li), and calcium (Ca) are impregnated inside the pores of the ACs and used for specific applications. As for example, silver, known for its antimicrobial and antiseptic properties, is impregnated in ACs and used as an absorbent in the purification of water.

Porous carbon or the activated carbon is coated with polymer. They can be used in hybrid circuits as thick film resistors, and nitrogen-rich porous carbon anode with high performance has been used in sodium ion batteries [61]. The porous carbon coated with polymer has also been used for hemoperfusion. Hemoperfusion is a treatment technique in which large volume of patient's blood is passed over an absorbent substance to remove toxic substances from blood. It has also been very popular in making special cloths and fibers used in personnel protection for the military. Charcoal hemoperfusion has been used to treat liver (hepatic) failure, various types of poisoning, and certain autoimmune diseases when coated with antigens or antibodies.

The degree of exhaustion of activated carbon bed is measured by the amount of milligrams of iodine solution absorbed by a gram of activated carbon. However, the use of iodine number as a measure of the degree of exhaustion of carbon bed can only be recommended if it has shown to be free of chemical interactions with the adsorbates. The iodine number of the activated carbon varies between 500 and 1200 mg/g. Typically, water treatment activated carbons have iodine numbers ranging from 600 to 1100 mg/g.

To evaluate a series of active carbons for their rates of adsorption, a method called decolorization of a standard molasses solution has been taken as a standard method, from which is derived the molasses number. Due to the size of color bodies, molasses number represents the potential pore volume available for larger absorbing species. A high molasses number indicates high adsorption of big molecules (within the range 100–600). Thus, given two active carbons with similar pore volumes for adsorption, the one having the higher molasses number will usually have higher feeder pores, resulting in a more efficient transfer of adsorbate into the adsorption space. It is interesting to note that the European molasses number is inversely related to the North American molasses number.

The iodine numbers and the molasses numbers are the indicators of the pore sizes. According to IUPAC (International Union of Pure and Applied Chemistry) definitions, three groups of pores are distinguished: (a) macropores (>50 nm), (b) mesopores (2–50 nm), and (c) micropores (<2 nm) [62]. Macropores and mesopores can be generally regarded as the highways into the carbon particle, and are crucial for kinetics, whereas micropores usually contribute to the major part

of the internal surface area. The pore size distribution in activated carbon is crucial for practical applications, such as adsorption of tannin, methylene blue, and dechlorination.

The desired pore structure, distribution of pores, specific surface area, texture, and specific adsorption are related to the surface functional groups [63–64]. It has been reported that the formation of a large number of basic and acidic groups on the surface of oxidized carbon to sorption and other properties can differ significantly from the unoxidized carbon [65–66].

The adsorption and desorption nature of the activated carbon enables it to work as a compressor and a heat pump in an adsorption refrigeration system. It consists of a solar collector, a condenser, and an evaporator placed in a refrigerator box. An activator soaked with methanol is placed inside the solar collector. During daytime, the solar collector is heated due to irradiation and the methanol is desorbed from the activated carbon. The methanol vapor thus desorbed from the activated carbon is condensed in the evaporator. At night, the collector temperature decreases to ambient temperature, and the activated carbon adsorbs the methanol from the evaporator. The liquid methanol in the evaporator vaporizes and absorbs heat from the water contained in the trays.

Figure 2.16 shows the schematic of desorption process and adsorption working principle. During desorption, the storage is charged, while it is discharged in the adsorption mode. Q in Fig. 2.16 represents energy (Des = desorption, Cond = condensation, Ads = adsorption, and Evap = evaporation). In an open sorption storage system, air transports water vapor and heat out of the packed bed of solid

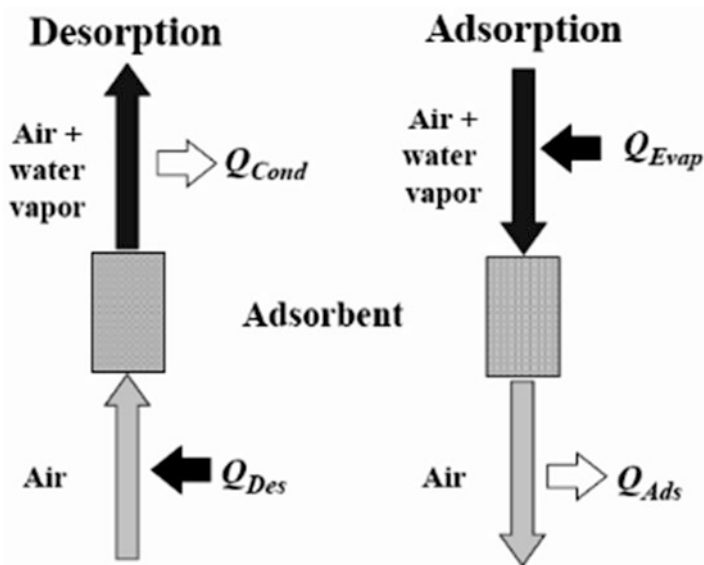


Fig. 2.16 Schematic of desorption process and the adsorption working principle. Q denotes energy (Adapted from F. Sadar, Theoretical heat pump)

absorbents. In desorption mode, a hot air stream enters the packed bed and desorbs the water from the adsorbent. The coefficient of performance (COP) can be defined as

$$\text{COP} = (\text{latent heat of assortment})/(\text{heat of desorption}) \quad (2.18)$$

Equation (2.18) defines the first system criteria in terms of adsorption materials. To fulfill the requirement, several criteria may exist, e.g., maximum cooling that can be achieved, the amount of heat that can be transferred, and the overall operating conditions of the heat pump. A large surface area is preferable for providing large adsorption capacity. Carbonaceous absorbents are nonpolar, and these absorbents have more affinity for oil and hydrocarbon than water.

Activated carbon, due to its adsorption nature, is used in the spill cleanup, drinking water filtration, air purification, and medical science. While it is useful in acute poisoning, it has been shown not to be effective in long-term accumulation of toxins, such as with the use of toxic herbicides. Ingestion of activated carbon has been a long-debated forum among the scientists. However, in the beginning of nineteenth century, it has been used in England as an antidote to flatulence and stomach trouble [67]. There is some evidence of its effectiveness to prevent diarrhea in cancer patients who have received irinotecan [68–69]. The Department of Energy (DOE) is exploring different possibilities of the use of nanoporous carbon, and the study of nanoporous carbon has been a fascinating field in modern materials science. Figure 2.17 shows the world's largest reactivation plant located at Feluy, Belgium.

Figure 2.18 shows a typical mobile adsorber on lorry from Chemviron, Belgium, and a typical adsorber unit from Donau carbon, Frankfurt, used in printing works. Both the Chemviron carbon, Feluy, Belgium and Donau carbon, Frankfurt, Germany, are the manufacturers of activated carbon (AC) and related materials.

2.1.6 Summary

Adsorption, catalysis, membrane separation, ion exchange, or process scale chromatography has played an important role in reducing the ecological load. There is no doubt that the modern adsorption technologies are rapidly improved and adopted to contemporary tasks of mankind. It is now widely accepted that the modern adsorption science is playing a dominant role in modern industry under environmental, economical, and energy-saving aspects. Adsorption-related domains have a major impact in many areas central to the question of our future, and in this context, it may be esteemed as the technology of the twenty-first century.

Application of solid adsorbents requires elaborate characterization of the material, which comprises determination of chemical composition, crystallographical and geometrical structure, surface and mechanical properties, as well as the shape and size distribution of the pores in porous materials. BET equation has been



Fig. 2.17 World's largest reactivation plant located at Feluy, Belgium (Photo Courtesy: Franck Honore, Creative Comm.,WIKI)



Fig. 2.18 A typical mobile adsorber on lorry and a typical adsorber in printing works (Photo Courtesy: Chemviron carbon and Donau carbon, & photo credit: D. Bathen)

accepted by IUPAC as the conventional method for determining the adsorbent surface area [70]. On the other hand, from the adsorption/desorption isotherms of nitrogen at 77 K, the suitable pore distribution can be calculated by means of Kelvin's equation. The specific surface area evaluation requires only a monolayer part of the adsorption isotherm, but the pore size distribution is measured by means of either the multilayer part of isotherm or in terms of mercury porosimetry.

On the basis of transformed desorption curves, it is possible to obtain the total pore volume of porous materials and pore size distribution curve (PSD) [71, 72]. Pore size distributions, mean pore radii, and the total pore volumes derived from thermogravimetric (TG) data are very similar to those calculated from adsorption isotherms measured at static conditions, especially from low-temperature nitrogen adsorption. Besides, methods based on density functional theory (DFT) and molecular simulations allow obtaining an accurate pore size analysis over the complete micropore/mesopore size range with a single method. The fundamental practical applications of adsorption and related domains are: separation and purification of liquid and gas mixtures, drying of gases and liquids before loading them into the industrial system, as well as removal of impurities from the liquid and gas media.

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